ADVANCES IN AGRONOMY

Academic Press is an imprint of Elsevier
525 B Street, Suite 1800, San Diego, CA 92101–4495, USA
225 Wyman Street, Waltham, MA 02451, USA
32 Jamestown Road, London, NW1 7BY, UK
The Boulevard, Langford Lane, Kidlington, Oxford, OX5 1GB, UK
Radarweg 29, PO Box 211, 1000 AE Amsterdam, The Netherlands

First edition 2013

ISBN: 978-0-12-407685-3
ISSN: 0065-2113

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Printed and bound in USA

13 14 15 16 10 9 8 7 6 5 4 3 2 1

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PREFACE

Volume 121 of *Advances in Agronomy* contains eight outstanding reviews dealing with technology advances, organic matter chemistry and composition, climate change, and crop and soil sustainability. Chapter 1 is an excellent and cutting-edge review on the use of NanoSims to study soil biogeochemical interfaces at fine scales. Chapter 2 details conservation practices to address climate change mitigation and adaptation. Chapter 3 is a comprehensive review of methodologies and techniques for analyzing soil organic matter over a range of spatial scales. Chapter 4 discusses the chemistry and biochemistry of organic components in rhizosphere soil solutions. Chapter 5 addresses ways to enhance agronomic productivity and carbon sequestration in soils of dryland ecosystems of India. Chapter 6 is a fine overview of constraints to crop production in the Middle East-West Asia region due to micronutrients. Chapter 7 covers beneficial interactions between plants, soils, and bacteria. These advances are discussed in the context of improving the yield and health of food and feed crops. Chapter 8 provides a thorough discussion of the buffer power concept and the important role it plays in African and Asian soils, with relevance to soil testing and nutrient availability.

I am most grateful to the authors for their first-rate reviews.

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CHAPTER ONE

Advances in the Analysis of Biogeochemical Interfaces: NanoSIMS to Investigate Soil Microenvironments

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Contents

Advances in Agronomy, Volume 121
ISSN 0065-2113
http://dx.doi.org/10.1016/B978-0-12-407685-3.00001-3

Abstract

Since a NanoSIMS high-resolution secondary ion mass spectrometry (SIMS) instrument was first used for cosmochemistry investigations over a decade ago, both interest in NanoSIMS and the number of instruments available have significantly increased. However, SIMS comes with a set of challenges that are of both technical and conceptual nature, particularly for complex samples such as soils. Here, we synthesize existing research and provide conceptual and technical guidance to those who wish to investigate soil processes at the submicron scale using SIMS, specifically with NanoSIMS. Our review not only offers advice resulting from our own operational experience but also intends to promote synergistic research on yet unresolved methodological issues. We identify and describe the basic setup of a NanoSIMS instrument, and important issues that may arise as a soil sample specimen are prepared for NanoSIMS analysis. This is complemented by discussions of experimental design, data analysis, and data representation. Next to experimental design, sample preparation is the most crucial prerequisite for successful NanoSIMS analyses. We discuss the requirements and limitations for sample preparation over the size range from individual soil particles to intact soil structures such as macroaggregates or intact soil cores. For robust interpretation of data obtained by NanoSIMS, parallel spatial, textural (scanning electron microscopy, atomic force microscopy), or compositional analyses (scanning transmission X-ray microscopy) are often necessary to provide necessary context. We suggest that NanoSIMS analysis is most valuable when applied in concert with other analytical procedures and can provide powerful inference about small-scale processes that can be traced via isotopic labeling or elemental mapping.

1. INTRODUCTION

1.1. The importance of nanoscale processes in soils research

Soil is often described as one of the most complex media on earth (Schulze and Freibauer, 2005). This complexity extends from the ecosystem scale to individual microaggregates, where nanometer-scale interactions between microbiota, organic matter (OM), and mineral particles are thought to control the long-term fate of soil carbon, nutrients, and pollutants (Lehmann et al., 2007; Schmidt et al., 2011). Processes that have a major impact at the landscape or global scale are determined by events occurring at the micro- and nanometer scales. For example, entrapment of soil organic matter (SOM) within microaggregates with a diameter of less than 250 μm and SOM sorption onto even smaller clay and iron oxides is a vital mechanism for long-term preservation of organic carbon (OC) in soils (Lehmann et al., 2007; von Lützow et al., 2006). Release of nutrients in the rhizosphere is

driven by root exudation at highly active micron-scale biogeochemical interfaces between roots, microbes, and minerals (Breland, and Bakken, 1991; Hinsinger et al., 2009; Norton and Firestone, 1996). Microbial activity occurs mostly in microhabitats (Dechesne et al., 2007; Müller and Défago, 2006; Nunan et al., 2007) and involves mineralization of SOM and organic pollutants. Hydrologic processes at the field scale are also influenced by fine-scale interactions as preferential flow paths may create localized zones of altered water and nutrient flow and thereby impact microbial abundance, community structure, and SOM turnover (Chabbi et al., 2009; Morales et al., 2010). Preferential flow zones are themselves heterogeneous at the microscale, with a heterogeneous supply of oxygen, water, and nutrients driving "hot spots" of microbial growth directly adjacent to areas of lesser microbial activity (Bundt et al., 2001). In all of these cases, activities at nano- to micron-scale soil biogeochemical interfaces determine the expression of higher level ecosystem functions. The majority of soil research, however, is conducted on bulk (>1 g) samples, which are often significantly altered prior to analysis. Pretreatments and analytical side effects include drying at varying temperatures, sieving/homogenization for process or elemental analysis, thermal alteration (as in pyrolysis GC/MS), or chemical alteration (as in alkaline extraction of "humic" substances or in cupric oxide oxidation for lignin analyses). With the advent of novel microspectroscopy and spectrometry techniques that allow for the study of micro- to nanoscale molecular, isotopic, and elemental patterns, it is now possible to make process-oriented observations (e.g., the stabilization of OM, sorption of pollutants, and mineral weathering) at the micron or submicron scale.

Elemental and isotopic imaging conducted via secondary ion mass spectrometry (SIMS) is a particularly promising technique for small-scale soil process research. SIMS uses a high-energy ion beam to sputter material from a sample surface, which can then be analyzed in a mass spectrometer. With high-resolution SIMS instruments (Cameca NanoSIMS 50, 50L, Gennevilliers, France), the distribution of elements and isotopes can be visualized with up to 50–150 nm lateral resolution within soil samples ranging from primary particles to subregions of intact soil cores. For this reason, NanoSIMS has the potential to provide quantitative measures of OM–mineral–microbial interactions and biogeochemical processing at the macro- and micro-aggregate or single-cell scale.

Relatively, few SIMS experiments have been conducted to date in soil science. In one of the first, Cliff et al. (2002b) used time-of-flight SIMS (ToF-SIMS) and additions of ^{15}N-labeled and ^{13}C-labeled compounds to

study small-scale differences in N assimilation as a function of C versus N limitation. When they compared SIMS values with bulk-measured microbial biomass N assimilation, they found substantial spatial heterogeneity in ^{15}N distribution that was not apparent through bulk analysis (Cliff et al., 2007). More recently, studies using SIMS and NanoSIMS analysis have revealed effects at even finer scales within individual microaggregates, mineral surfaces, microbes, and root hairs (Blair et al., 2006; Cliff et al., 2002a; Clode et al., 2009; DeRito et al., 2005; Herrmann et al., 2007a,b; Keiluweit et al., 2012; Pumphrey et al., 2009). An early review paper by Herrmann et al. (2007b) focused on potential applications for soil ecology and included the first application of the NanoSIMS technique with an intact soil microaggregate. Subsequent publications have addressed the technical aspects (sample preparation) and investigations of organo-mineral associations at scales ranging from clay size mineral grain to intact soil cores (Keiluweit et al., 2012; Mueller et al., 2012b; Remusat et al., 2012).

In this chapter, our goal is to provide insight into the range of potential NanoSIMS applications in soil system research, discussing technical capabilities and limitations, major sample requirements, and important complementary microspectrometry techniques. As NanoSIMS applications in closely related fields, such as plant science and microbiology, have been reviewed recently (Moore et al., 2011a; Musat et al., 2012), we focus on the use of NanoSIMS in soil research.

1.2. Fundamentals of SIMS

SIMS is a surface analysis technique for solid samples. Primary ions, with a kinetic energy ranging from a few hundred electron volts to tens of thousands of electron volts, are focused on the sample surface, ejecting atoms and molecules in a process called sputtering (see Fig. 1.1). A small fraction of the ejected atoms and molecules is ionized and can be extracted with an electrostatic field into a mass spectrometer. The fraction of the sputtered material that is ionized is determined by the ionization efficiency of the element in the sample matrix and is referred to as the secondary ion yield. For different elements, secondary ion yields vary over many orders of magnitude and also strongly depend on the physicochemical nature of the sample (Storms et al., 1977; Wilson et al., 1989). Within the mass spectrometer, secondary ions can be separated according to their mass to charge ratio in a quadrupole, magnetic sector, or time-of-flight (TOF) mass analyzer. These analyzers differ in terms of detectable mass range, sensitivity, ion transmission, and cost. As NanoSIMS has both high sensitivity and spatial resolution

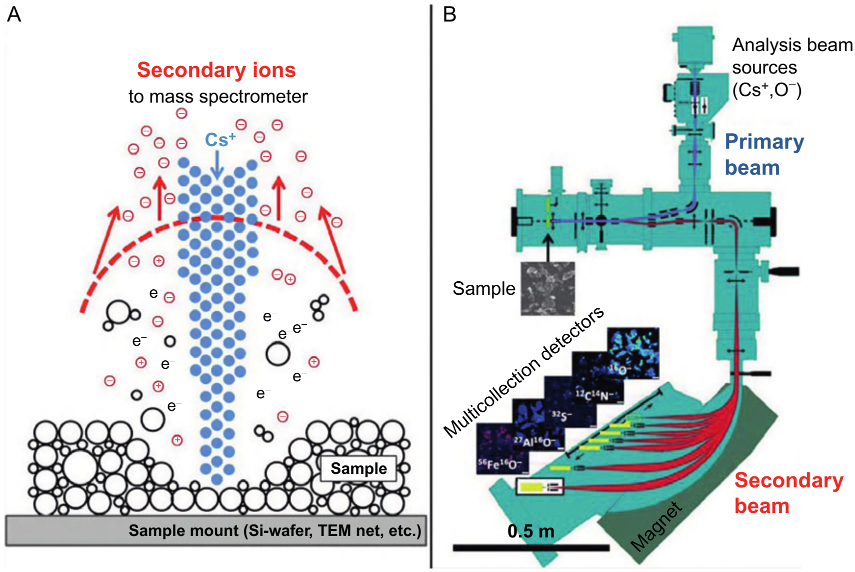

Figure 1.1 (A) coaxial setup of the NanoSIMS, indicating the primary and secondary ion beam in relation to the sample surface. Due to the coaxial setup, the secondary ions must have the opposite charge from the primary ions to enable extraction to the mass spectrometer. (B) Schematic of the NanoSIMS, with the primary ion beam in blue and the secondary ion beam in red *Courtesy of Cameca (Gennevilliers, France), adapted from Myrold et al. (2011). Reprinted from Myrold et al. (2011), Copyright (2012), with permission from Elsevier.*

at high mass resolving power, this particular SIMS instrument meets many of the specific requirements for microscale elemental and isotopic mapping analyses in soil science.

1.2.1 NanoSIMS

The NanoSIMS is optimized for SIMS imaging with submicron lateral resolution. The NanoSIMS 50 and 50L instruments, conceived by Slodzian (Slodzian, 1987; Slodzian et al., 1992), were designed by Bernard Daigne, François Girard, and François Hillion (Hillion et al., 1993) and manufactured by Cameca France under a license from the Office National d'Études et de Recherches Aérospatiales at Université Paris-Sud (UPS ONERA). There are now more than 30 NanoSIMS instruments installed worldwide, working on a wide range of applications ranging from geology and cosmochemistry (Floss et al., 2006; Hoppe, 2006; Stadermann et al., 1999; Wacey et al., 2010a) to biology (Finzi-Hart et al., 2009; Kraft et al., 2006; Lechene

et al., 2006), material science (Valle et al., 2011), and soil science (Herrmann et al., 2007a; Keiluweit et al., 2012; Mueller et al., 2012b).

The key innovation of the NanoSIMS is the coaxial lens (Fig. 1.1) which focuses the primary ion beam and extracts and focuses the secondary ion beam as well. This configuration minimizes the distance between the sample surface and primary focusing lens, allowing the primary beam to be focused to a much smaller diameter than in conventional SIMS instruments. In addition, the secondary mass spectrometer is optimized for high transmission at high (>3000) mass resolving power. The NanoSIMS comes equipped with a Cs^+ primary ion source for analysis of negative secondary ion species (e.g., $^{12}C^-$, $^{13}C^-$, $^{12}C^{14}N^-$, $^{12}C^{15}N^-$, $^{28}Si^-$, $^{27}Al^{16}O^-$, and $^{56}Fe^{16}O^-$) and an O^- primary beam source, for analysis of positive secondary ions (e.g., $^{23}Na^+$,$^{39}K^+$, $^{44}Ca^+$, ^{56}Fe). Due to the coaxial lens setup (Fig. 1.1B), secondary ions must have the opposite charge from primary ions to enable extraction to the mass spectrometer. A ~150 nm diameter Cs^+ primary ion beam with a beam current of 1–2 pA can routinely be achieved. While an even smaller beam diameter is possible, there are trade-offs between high-resolution (with reduced beam current) and secondary ion count rates. Higher currents and thus beam diameters are often crucial to yield significant amounts of secondary ions (e.g., $^{13}C^-$, $^{12}C^{15}N^-$, $^{56}Fe^{16}O^-$) when analyzing soil samples. With an O^- beam, a diameter of ~400 nm is typical.

The advantage of the NanoSIMS instrument lies in the coupling of a continuous, high spatial resolution analysis beam with high mass resolving power, resulting in high sensitivity and specificity with relatively short integration times. Users should also be fully aware that the NanoSIMS 50 and 50L are both "dynamic" SIMS instruments where the sample is actively eroded during the sputtering process and molecular bonds are broken by the primary ion beam. Up to five (NanoSIMS 50) or seven (NanoSIMS 50L) secondary ions can be detected simultaneously. Additionally, if operated in Cs^+ mode, secondary electrons produced by the collision cascade can be detected by a photomultiplier, providing a secondary electron image that can provide structural and textural information that is comparable to a low-resolution scanning electron microscopy (SEM) micrograph.

1.2.2 Basic requirements for NanoSIMS samples

A wide range of solid samples are compatible with SIMS, provided they are dry and stable under high vacuum (<10^{-9} mbar), relatively flat (<2–30 μm of relief), and conductive. Sample out-gassing can be caused by absorbed

water, other volatiles, hydrocarbons, or samples prepared via resin embedding. Pretreatment in a vacuum oven under low heat can reduce out-gassing within the analysis chamber. Out-gassing may degrade analysis conditions by elevating chamber pressure, reducing ion transmission, and generating molecular interferences or physical contamination, which will all lead to poor analysis quality. Sample flatness is also important as any surface roughness may influence sample sputtering, ion extraction, and mass spectrometer tuning. For natural abundance isotopic ratio measurements, 2–4‰ level external precision can be achieved with repeated analyses of bacterial spores with ~1 μm of relief (P.K. Weber, unpublished results). For isotopic tracer experiments, more topographic relief (10–20 μm) can be tolerated (Woebken et al., 2012). Even higher topographic relief (~30 μm) may also be viable in some applications (P.K. Weber, unpublished results) but with significant loss in precision and the need for careful monitoring of measurement quality. Finally, because SIMS uses an ion beam to eject charged ions from the sample's upper atomic layers, a mechanism to dissipate charge from the analysis location is critical. In our experience, most soil samples are semi-insulating and typically must be coated in an evaporator or sputter coater with a 2–20 nm layer of gold (or carbon, iridium, gold–palladium, or platinum) to minimize charging during analysis. Sample flatness can also interact with charge dissipation characteristics. As a general rule, the more topography a sample has, the thicker a conductive coat needs to be to bridge topographic gaps. Metal coating and sample flatness become particularly important if an electron flood gun is to be used for charge compensation (see NanoSIMS soil preparation details below).

2. EXPERIMENTAL APPROACHES FOR THE STUDY OF SOIL MICROENVIRONMENTS USING NanoSIMS

2.1. Lessons learned from geology and microbiology

Perhaps one of the most appealing aspects of NanoSIMS analysis for many soil scientists is the instrument's potential to quantitatively localize stable isotopes at a previously unresolved spatial scale. Since the fields of geology, cosmochemistry, and geomicrobiology have a more extensive tradition with SIMS and NanoSIMS applications, that literature is a logical source of illustrative models for soils research. Cosmochemists were first to use NanoSIMS for isotopic measurements, taking advantage of its high spatial resolution and simultaneous imaging capabilities. Using NanoSIMS, Messenger et al. (2003) located rare isotopically anomalous (>100‰) micron-sized presolar

grains within meteoritic samples that are too small to have been analyzed by bulk measurements or even conventional SIMS (e.g., Cameca SIMS 1280). NanoSIMS has also been used to measure large isotopic fractionation in biominerals (e.g., carbonates from mollusk shells and corals) and deduce metabolic pathways such as methanotrophy (Rasmussen et al., 2009) or sulfate reduction and sulfur disproportionation (Philippot et al., 2007; Wacey et al., 2010b). In geologic samples, NanoSIMS imaging was employed to support a microbial origin for Ooids—concentrically laminated sedimentary grains found in turbulent marine and freshwater environments (Pacton et al., 2012) and a microbial role in Fe mineralization within spheroidal iron oxide concretions associated with paleoaquifers (Weber et al., 2012).

All of the studies mentioned above capitalized upon natural isotope fractionation effects that can shift natural abundance values by 10s to 100‰ (e.g., for biological sulfur cycling −8.5‰ to +19‰ $\delta^{34}S_{CDT}$ (CDT, Canyon Diablo troilite) and for methanotrophy -55‰ to -43‰ $\delta^{13}C_{PDB}$ (PDB, Pee Dee belemnite) (Rasmussen et al., 2009)). These effects are in many cases significantly larger than those found in soil/sediment systems, where prominent isotopic effects range from ~1‰ to 11‰ $\delta^{13}C$ (litter decomposition, C3–C4 plant shifts; Ehleringer et al., 2000), ~7‰ $\delta^{15}N$ (soil depth gradients; Billings and Richter, 2006), or as little as 0.8‰ $\delta^{56}Fe$ (soil iron pools; Kiczka et al., 2011). One exception is the work of Orphan et al. (2001), who have used SIMS and NanoSIMS to image isotopic fractionation in modern anoxic sediment cores of the Eel river basin in the Pacific Ocean. There, the authors report isotopic fractionations of $\delta^{13}C$ of up to −96‰ in the interior of bacterial aggregates, indicating consumption of isotopically light methane by methanotrophic bacteria.

For most soil process-level questions, the best approach may be to use stable isotope labeling as a way to document transformation pathways in soil microenvironments over time. This approach, like many of the published examples in cosmo- and geochemistry, would take full advantage of the NanoSIMS's spatial resolution while improving detection of the isotopic species of interest. In the past decade, stable isotope labeling (often with ^{13}C or ^{15}N) and NanoSIMS analyses have been widely used in environmental microbiology, supporting research on the metabolism of single microbial cells (Pett-Ridge and Weber, 2012) both in pure culture and in natural environmental samples ranging from marine bacterial and archaeal communities (Dekas et al., 2009; Halm et al., 2009; Musat et al., 2008; Ploug et al., 2010), to acid mine drainage biofilms (Moreau et al., 2007), to ^{13}C and ^{15}N fixation in diazotrophic cyanobacteria (Finzi-Hart et al., 2009;

Popa et al., 2007; Woebken et al., 2012) and eukaryotes (Lechene et al., 2006, 2007).

An idealized stable isotope-labeling experiment in soil might proceed as follows: (1) add an organic compound of interest, labeled for instance with ^{13}C or ^{15}N, to a model system that contains reactive mineral surfaces and an active microbial decomposer community; (2) incubate under controlled conditions, varying an edaphic variable of interest (moisture, temperature, pH); (3) prepare and analyze samples via NanoSIMS imaging to determine the physical fate of the target compound whether it becomes metabolized (and the label is transferred to microbial decomposers) or whether it is adsorbed to mineral surfaces. Enrichment of the label above a background value could then be used to support inference about the fate of the compound of interest. This type of application could potentially contribute to both studies of soil carbon turnover dynamics and investigations of contaminant fate in soils.

Previous NanoSIMS studies of biotic (microorganisms and plants) and abiotic materials (minerals, fossils) represent endmember models of the soil system, with its inherent combination of geologic and microbiological aspects. This substantial literature serves as a valuable resource for soil scientists interested in designing microscale soil research, particularly as a resource for experimental concepts and sample preparation protocols. In the following section, we discuss examples from soil science where NanoSIMS has been successfully applied, as well as additional areas where soil interface research could significantly benefit from high-resolution isotopic imaging in the future. As we point out potential applications, we also mention pitfalls and methodological constraints.

2.1.1 Investigating mineral–organic associations

Historically, studies of mineral–organic associations have employed bulk analysis procedures performed on operationally defined physical fractions (Balesdent et al., 2000; Christensen, 2001; Eusterhues et al., 2005; Schöning et al., 2005). The goal of such procedures is to isolate mineral–organic associations of given characteristics, such as an increasing proportion of microbially processed OM in fractions of increasing density (Derrien et al., 2006; Grandy and Neff, 2008; von Lützow et al., 2007). In contrast to bulk analysis, NanoSIMS offers the possibility to examine organo-mineral assemblages in the context of intact spatial structures. If a stable isotope-labeling experiment (see above) is used, NanoSIMS images can potentially reveal the spatial distribution and dilution of a tracer material as it moves into the

soil matrix. They can also reveal whether preferential associations of certain OM types predictably associate with certain mineral phases. This is possible because of three main advantages of NanoSIMS over other microscopic techniques: (1) elemental mapping can be done with better lateral resolution, (2) the low depth penetration (~10–20 nm) of the NanoSIMS primary beam allows thin surface layers to be examined, and (3) highly accurate isotope detection allows the operator to track OM ^{13}C and OM ^{15}N onto distinct minerals in an intact micro-environment and thus enables process-level studies. In a proof-of-concept example, these three advantages were exploited by Heister et al. (2012), who showed that in artificial soil mixtures, soil minerals, and organic materials can be distinguished in NanoSIMS images, using the distinction between organic material-derived ions ($^{12}C^-$ and $^{12}C^{14}N^-$) and mineral-derived ions ($^{28}Si^-$, $^{27}Al^{16}O^-$, and $^{56}Fe^{16}O^-$). The authors used NanoSIMS in this study as a tool for microscale elemental mapping of OM on mineral surfaces. They showed that OM tended to be attached to phyllosilicate clays in the form of isolated patches, while continuous coatings of OM enveloped small ferrihydrite particles. Such microscale heterogeneities could not have been resolved by SEM/EDX (energy-dispersive X-ray spectroscopy) measurements. In another example, Mueller et al. (2012b), working with resin-embedded soil macroaggregates, found heterogeneous isotopic enrichment at the microscale following the application of a $^{13}C/^{15}N$ label (amino acid mixture of algal origin) to natural soils. They speculated that microbial activity may have lead to the increased utilization of freshly added OM or that soil components have different sorption capacities. The NanoSIMS's unique capacity to detect stable isotope tracers at the microscale enabled both these studies to confirm the predicted physical dimensions of organo-mineral associations.

By combining isotopic and elemental imaging, NanoSIMS analysis can also reveal whether certain OM types predictably associate with certain mineral phases. This particular capacity of the NanoSIMS was used by Keiluweit et al. (2012) in a study where $^{13}C/^{15}N$-enriched fungal hyphal extracts were incubated with organic horizon soil. NanoSIMS images of ^{15}N enrichment and iron distribution suggest that nitrogen from fungal cell walls was rapidly and preferentially deposited as thin organic coatings onto Fe (hydr)oxide surfaces (Keiluweit et al., 2012). Further analysis of these samples by scanning transmission X-ray microscope in combination with near edge X-ray absorption fine structure spectrometry (STXM–NEXAFS) revealed that these soil microstructures were enriched in aliphatic C and amide N, suggesting that a concentration of microbial lipids and proteins had quickly

become associated with Fe (hydr)oxide surfaces. Remusat et al. (2012) used a similar approach to image intact soil particles with low levels of isotopic enrichment sampled 12 years after a ^{15}N litter-labeling experiment in a temperate forest. They describe microsites of isotopic enrichment ("^{15}N hot spots") on mineral surfaces, and in one microsite, they suggest that ^{15}N enrichment was also linked to the presence of microbial metabolites. This kind of combined approach, NanoSIMS image analysis joined to complementary microscopy (SEM–EDX, STXM/NEXAFS), may be a particularly profitable means to infer the molecular and spatial fate of labeled organic materials in a mineral matrix and has the potential to contribute to a mechanistic understanding of sorption, occlusion, and decomposition processes that operate at fine spatial scales.

A recent quantitative analysis of organo-mineral assemblages by Hatton et al. (2012) used a combination of macro- and microscale analyses for an internal calibration of C/N and $^{15}N/^{14}N$ ratios in sequentially separated soil density fractions. This approach is based on the assumption that macroscopic features, visible under reflectance light microscope and analyzable by elemental analyzer isotope ratio mass spectrometry (EA-IRMS), are also found at the microscale as detected in SEM or NanoSIMS images. The authors collected NanoSIMS images over 500 μm^2 for each density SOM fraction and corrected these using EA-IRMS data from macroscopic features. Because matrix-matching SIMS standards for SOM do not yet exist, this calibration approach is a promising step toward a better quantification of data derived from SIMS images. While significant procedural challenges remain, the examples presented above illustrate how well-designed experiments can benefit from NanoSIMS information to help decipher chemical and microbiological processes in soil microenvironments.

2.1.2 *Investigating intact three-dimensional microstructures*

NanoSIMS imaging may also be profitable in studies of microscale soil architecture. The first systematic approach to the study of *in situ* soil features was established by the micropedological work of Kubiena (1938). Whole intact soil clods were impregnated with epoxy resin, thin sections were produced, and small-scale pedological features were studied using transmitted light microscopy. A large range of soils have been studied using this technique, combining different light sources ranging from polarized light to fluorescent staining of microbial cells (Bullock and Murphy, 1980; Eickhorst and Tippkoetter, 2008; Fisk et al., 1999; Li et al., 2004; Pulleman et al., 2005). With the rise of analytical techniques that can resolve soil features

at the nano- to microscale (e.g., transmission electron microscopy, TEM; atomic force microscope, AFM; NanoSIMS), the micromorphological examination of soils is experiencing a renaissance. However, mineral particles pose a challenge to elemental mapping and isotope tracing experiments in intact soil matrices because they make embedding and thin sectioning more difficult and can cause electrical charging effects (Cliff et al., 2002b; Pett-Ridge et al., 2012). Still, a number of proof-of-concept studies have successfully shown that ^{15}N and ^{13}C isotope additions can be imaged by NanoSIMS in two dimensions within a natural or synthetic soil matrix (Herrmann et al., 2007b; Keiluweit et al., 2012; Mueller et al., 2012b; Pett-Ridge et al., 2012; Remusat et al., 2012).

Sample preparation is the most important issue to be resolved prior to microscale studies of soil three-dimensional structures. This is particularly true for soil macroaggregates (>250 μm in diameter) which have topography too large for reliable NanoSIMS measurements. To maintain adequate flatness and integrity in friable samples, larger soil aggregates and intact soil cores will typically require embedding and subsequent sectioning. However, simply cutting large aggregates into sections can affect structural integrity. One solution is thin sectioning, although the approach used must be chosen with the target ions in mind. The most important considerations include the following:

Does the sample contain both mineral and organic phases?

Might the embedding medium dilute the signal of the target species (e.g., ^{13}C)?

Is *in situ* hybridization to be used, and are diffusible ions or molecules of interest?

We discuss the finer details of these concerns in Sections 3.4.2 and 3.4.3. In general, our experience has shown that for smaller macroaggregates (~250 μm) cryosectioning is a laborious but worthwhile technique to obtain cross sections while avoiding contamination with any artificial C or N sources. For examination of whole intact soil cores or macroaggregates (several mm in diameter), resin embedding is currently the best option, although it introduces an artificial C and N source, which can interfere with both isotopic analyses and techniques to determine the chemical structure of OM (e.g., STXM). If target ions include C and N, resin embedding should thus be used only for larger volume soil specimens consisting of a friable porous network of organic and mineral particles that have to be tightly bound together in order to allow cross sectioning and polishing. However, for some resins (e.g., Araldite 502), the ^{12}C^{14}N/^{12}C ratio allows to

distinguish between sample OM and embedding agent (Weber et al., 2012). The resin embedding approach has been used to prepare slices of intact soil cores for elemental mapping of *in situ* interfaces in a buried Oa horizon originating from a permafrost-affected soil in Northern Alaska (Typic Aquiturbel, coastal plain near Barrow) (Fig. 1.2). In this case, NanoSIMS imaging was used for elemental mapping of natural microscale features at a scale which could not be resolved by comparable techniques such as SEM–EDX. This example shows how NanoSIMS can illustrate the

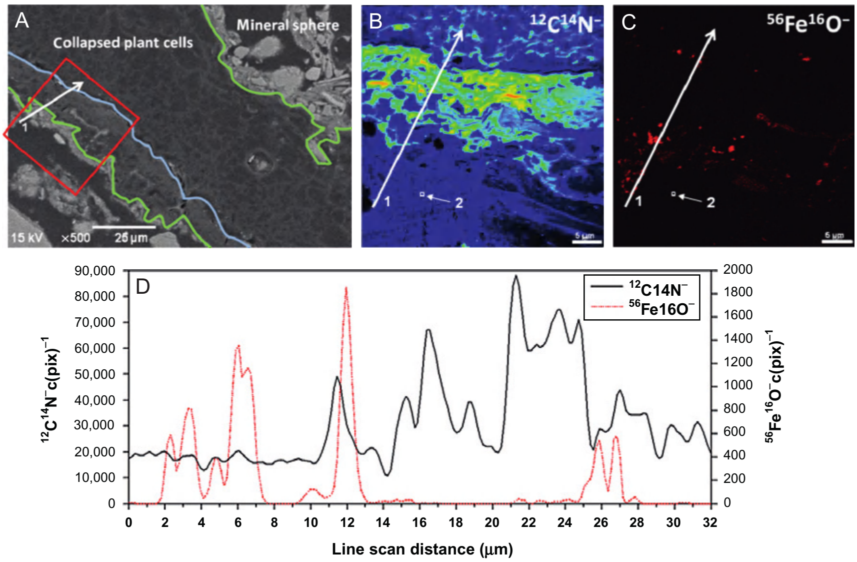

Figure 1.2 Micrograph and microanalysis of an embedded cross section derived from a Cryosol soil core (Oa horizon, Typic Aquiturbel) from Barrow, Northern Alaska. (A) Backscatter electron image recorded with a SEM. (B and C) NanoSIMS images ($^{12}C^{14}N^-$ and $^{56}Fe^{16}O^-$) recorded with a NanoSIMS 50L at TU München. The backscatter SEM image shows collapsing plant cells of particulate OM in the center surrounded by mineral spheres. The red square in the SEM image indicates the area analyzed by NanoSIMS, the green line indicates the interface between particulate organic matter and mineral phase, and the blue line depicts the boundary between totally and partly collapsed plant cell structures. The NanoSIMS images indicate the distribution of organic matter ($^{12}C^{14}N^-$) and the iron distribution ($^{56}Fe^{16}O^-$) within the plant cell region and suggest organo-mineral interfaces in the early stages of formation. (D) Line scan data derived from analysis of NanoSIMS $^{12}C^{14}N^-$ and $^{56}Fe^{16}O^-$ secondary ion images. The line scans demonstrate the spatial distribution of both secondary ion species along a transect, illustrating the iron clusters within the organic matter region. An area of 0.5–0.5 μm (square #2 in images) in size was scanned along the transect. *C. W. Mueller (unpublished data).*

patterning of distinct phases (OM ($^{12}C^{14}N^{-}$), organo-mineral interfaces, plant cells) via elemental mapping of such friable and highly heterogeneous intact soil structures.

2.1.3 Investigating plant–soil processes

The interfaces between plant roots and soil (rhizosphere) or fungal hyphae and minerals (hyphaesphere) are extremely biologically active and important sites for mineral weathering (Finlay et al., 2009). Hinsinger et al. (2009) suggest that a lack of suitable observational tools stands in the way of a better understanding of microscale elemental distributions in the rhizosphere. Here, NanoSIMS might well fill the gap between reflectance light microscopic (e.g., epifluorescence, polarized light) and X-ray techniques (e.g., X-ray tomography) to trace C, N, and nutrient transfers between roots, microbes, and soil. For the biotic side of the plant–soil system, Gea et al. (1994) showed the utility of SIMS by imaging Ca in ectomycorrhizal fungi (*Hebeloma cylindrosporum*) associated with pine trees (*Pinus pinaster*). Figure 1.3 is a proof of concept of how NanoSIMS may be used to explore an intact plant–soil system at the microscale. In this example, a French oak (*Quercus robur*) seedling was grown in a vermiculite/soil mixture with a mycorrhizal fungi *Piloderma croceum* in order to track interfaces between mineral constituents and the plant root. NanoSIMS images of an embedded oak root tip illustrate that clay minerals may be distinguished from root cells and mycorrhizal cells within the vermiculite layers, revealing the interfaces between the mineral soil compartment, roots, and mycorrhizal fungi. This example demonstrates how NanoSIMS images might contribute to the exploration of intact plant–soil microbe interfaces.

Part of the difficulty associated with attempts to image the interfaces between plants, microbes, and mineral particles has to do with preparing samples in a manner that adequately preserves these interfaces. A challenging but promising approach to preserve intact soil architecture was demonstrated by Clode et al. (2009) who prepared 100 nm thick cross sections of ^{15}N-labeled wheat roots and associated bacteria by slowly infiltrating with araldite epoxy over the course of several days. The resulting epoxy blocks were thin-sectioned and then observed by both TEM and NanoSIMS at the University of Western Australia. The TEM images clearly identified bacteria attached to the cortical cell walls, while NanoSIMS imaging revealed that not all of the bacteria had incorporated the ^{15}N label (Fig. 1.4). While it is possible that some cells were not metabolically active or dead, it is equally possible that some of the ^{15}N "hot spots" were actually remnant effects of salts derived from

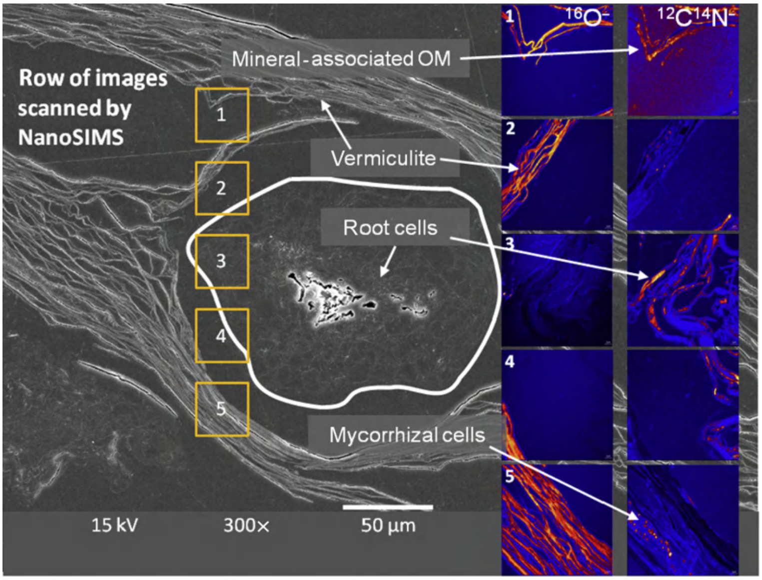

Figure 1.3 Back-scattered secondary electron micrograph and NanoSIMS ion images ($^{16}O^-$, $^{12}C^{14}N^-$) of an embedded root tip cross section prepared from a French oak root (*Quercus robur*, clone DF159 infected with mycorrhizal fungi *Piloderma croceum*, courtesy of F. Buscot, UFZ Halle, Germany and T. Grams, TU München, Germany) grown in a vermiculite/soil mixture. The root and adhering rhizosphere soil was fixed according to Karnovsky (1965), embedded in an epoxy resin, cross sectioned, polished, and imaged via NanoSIMS. The $^{16}O^-$ NanoSIMS images illustrate thin clay mineral layers, whereas the $^{12}C^{14}N^-$ ion images indicate the location of root cells. The row of yellow squares in the SEM image show where NanoSIMS analyses occurred in a transect across the interfaces between root, mycorrhizal fungi, and mineral particles. *C. W. Mueller (unpublished data).*

the enriched precursor material ($(^{15}NH_4)_2SO_4$). This is a case where a complementary technique, for example, fluorescent *in situ* hybridization (FISH) or a live/dead or DAPI stain (see Section 4.4), might be useful to corroborate whether enriched features in NanoSIMS images truly are bacterial cells.

2.1.4 Tracking organic and inorganic pollutants

Organic and inorganic pollutants span a wide range of molecular properties and may be involved in a host of mechanistically different interactions with soil solids. Important inorganic pollutants are metals and metalloids (e.g., Pb, As) (Bradl, 2004; Wilson et al., 2010; Zimmer et al., 2011), including radioactive particles from nuclear accidents (Carbol et al., 2003; Spezzano, 2005).

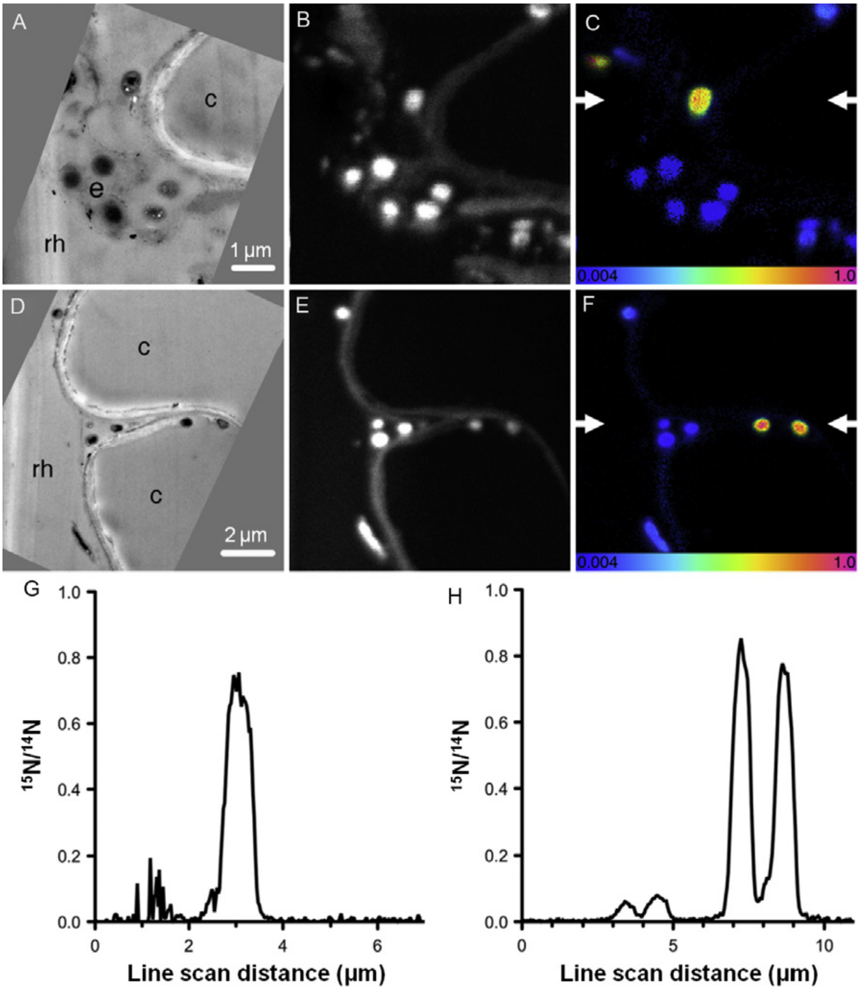

Figure 1.4 TEM and NanoSIMS images of wheat roots (*Triticum aestivum*) exposed to ^{15}N for 24 h. The samples were fixed with 2.5% glutaraldehyde in 0.1 M phosphate buffered saline and dehydrated in a graded series of acetone. The roots were infiltrated in acetone araldite mixtures over several days, using a gradually increasing araldite concentration. Final embedding in Araldite 502 was done according to Herrmann et al. (2007a). Embedded samples were cut into slices, reembedded in 10 mm mounts, and polished using silicon carbide paper and finally diamond paste. TEM images (A and D) show the presence of microorganisms in the rhizosphere (rh) and extracellular mucilage matrix (e) adjacent to the root cells (c). NanoSIMS images (B and E) of the same regions show organic matter distribution recorded as $^{12}C^{14}N^{-}$. NanoSIMS ratio images (E and F) of $^{15}N/^{14}N$ (natural abundance at 0.004) confirmed the ^{15}N enrichment of some microorganisms. Line scan data from the regions between the arrows (in C and F) is shown in (G) (from C) and H (from F). *Adapted from Clode et al. (2009). Republished with permission of American Society of Biologists (www.plantphysiology.org), Copyright 2012, permission conveyed through Copyright Clearance Center, Inc.*

Organic pollutants are inherently more diverse, encompassing the full range from nonpolar polycyclic aromatic hydrocarbons to relatively polar chlorinated hydrocarbons and polychlorinated biphenyls. To date, SIMS has been used to study the microscale distribution of metals (e.g., Cd, Cr), metalloids (e.g., As), and halogens and organic pollutants in microbial cells (Eybe et al., 2008), plants (Lombi et al., 2011; Mangabeira et al., 2006; Martin et al., 2001; Migeon et al., 2009; Moore et al., 2010, 2011b; Tartivel et al., 2012), animals (Eybe et al., 2009), and human tissues (Audinot et al., 2004). NanoSIMS has been used to examine plutonium transport in the subsurface of heavily contaminated sites (parts per million levels) (Kips et al., 2012; Novikov et al., 2006). When there is substantial contamination, Pu can be directly imaged *in situ* and the association of Pu with specific minerals can be determined to constrain transport mechanisms. An intriguing example of a system comparable to primary soil particles (e.g., clay minerals, OM particles) was presented by Krein et al. (2007), who located heavy metal accumulation in aerosols using NanoSIMS by imaging $^{63}Cu^{-}$, $^{75}As^{-}$, $^{118}Sn^{-}$, and $^{123}Sb^{-}$. This work suggests that it is possible to determine spatial dependencies between OM and inorganic pollutants and evaluate "hot spots" on micron-scale particles.

The primary limitations for NanoSIMS studies on organic pollutants are the vapor pressure of the target pollutants (e.g., nonvolatile organic compounds), the concentration of the target, and incorporating a tracer for the target. Eybe et al. (2008) embedded *Anabaena* sp. cells grown on the pesticide deltamethrin in an epoxy resin. To trace the pesticide within the embedded cells, $^{81}Br^{-}$ was imaged in the NanoSIMS, illustrating how halogen containing pollutants may be used as tracers within biological samples. Another example is the work of Tartivel et al. (2012), who traced bromotoluene by the imaging of $^{81}Br^{-}$ in chemically fixed plant roots (*Hedera helix*) and resin-embedded soil cross sections.

3. NanoSIMS REQUIREMENTS FOR SOIL-RELATED STUDIES

3.1. Technical considerations for soil samples

With its improved primary ion optics and secondary ion transmission at high mass resolving power, the NanoSIMS 50 and 50L enable SIMS analysis at the nanometer scale. However, there are specific technical limitations that the potential user must consider, especially for soils applications. While primary beams smaller than 50 nm are possible with idealized samples, the

number of ions collected from the impacted volume starts to fall below the useful level in soils. NanoSIMS is a high vacuum ($\sim10^{-10}$ Torr) instrument that requires samples to be dehydrated, conductive and have low topography (ideally submicron for natural abundance and <30 μm scale for isotopic enrichment experiments). As a result, live microbial cells cannot be tracked, and to measure process effects over time, one must rely on subsampling and replication. Samples should be fixed and can be thin-sectioned to achieve a flat surface, ideally without rearranging the locale of target elements or molecules. While not currently available, a cryogenic stage might allow frozen samples to be analyzed, thereby preserving them in a more natural state.

Though analyses of natural abundance ^{13}C and ^{15}N are widely used in soil science, the NanoSIMS is capable of measuring isotope ratios with a precision of ~1‰ only in very favorable cases, and even a level of ~10‰ precision is likely to be very challenging to achieve in most complex soil samples. To obtain such a high precision (<1‰), relatively large amounts of material must be extracted from the sample surface (nanograms), requiring a large primary spot size ~20–30 μm. Such a spot size might itself exceed the microscale structures of interest (e.g., bacterial cells, clay minerals). Also, the much smaller primary beam used in NanoSIMS imaging generates a smaller number of secondary ions, necessitating the use of electron multiplier (EM) detectors. EMs have a faster response time than faraday cup (FC) detectors (commonly used in larger beam SIMS instruments) and are thus both fast enough and provide sufficient dynamic range for imaging. EM detectors are, however, subject to a number of artifacts (limited count rates and detector aging) that effectively limit the precision to about 1‰. On top of this, the extraction conditions from location to location can be hard to maintain at a level that yields precision better than one part in a thousand, especially with heterogeneous, samples such as soils. The limitations on precision mean that in most soil systems, natural abundance measurements will not produce useful data. Isotopic measurements with higher precision can be achieved using the Cameca IMS1280, a large geometry magnetic sector ion probe, combining high transmission, high abundance sensitivity, and high density of the primary beam with thermally insulated FC electronics. This instrument could potentially be used in complementary studies with a NanoSIMS to record images of high spatial resolution as well as per mil level precision.

In our experience, tracking of isotopically labeled tracers is probably the most practical way to explore microscale soil processes using NanoSIMS (Herrmann et al., 2007a; Keiluweit et al., 2012). As C and N are the key elements in OM studies, substrates enriched in ^{13}C and/or ^{15}N are regularly

used for general investigations of microbial metabolism in soils as well as for the more specific purpose of following the fate of organic compounds as they cycle through soils (Kuzyakov et al., 2000; Ruetting et al., 2011). Of critical importance in tracer studies is whether the labeled substrate becomes chemically modified or is otherwise affected by the sample preparation. The potential user is reminded that NanoSIMS is not well suited for the identification of molecules or characteristic molecular fragments and so will rarely be able to address this kind of problem directly.

While quantitative NanoSIMS isotopic analyses are relatively straightforward, quantitative analyses of elemental abundances are considerably more challenging. In the fields of material science and mineralogy, SIMS users usually employ standards to correct for differences in yields and quantity for defined element–matrix combinations. The inherent complexity and variability of soil matrices can complicate this approach, as appropriate standards are harder to obtain or manufacture. The C to N elemental ratio in soil OM, for example, is of general interest to soil scientists. The measurement of this ratio is inherently challenging because $^{12}C^{-}$ has a different formation mechanism than the $^{12}C^{14}N^{-}$ ion (N is detected as CN), as atomic N ionization is very poor. As a result, the yield of the two species can change relative to each other during the course of an analysis. C to N ratio measurements are therefore very challenging, requiring matrix-matched standards and method optimization, and ultimately may result in measurements of low accuracy and precision. It is an open question whether the heterogeneity of soil material makes such measurements additionally challenging.

3.2. Sample documentation

To facilitate the analyses, it is best to determine regions of interest (ROIs) on the sample prior to performing NanoSIMS measurements (Herrmann et al., 2007a; Moore et al., 2011a; Weber and Holt, 2008). Sample mapping can greatly enhance the efficiency of the analyses and is often critical to interpretation of results. Most SIMS instruments have the equivalent of an epi-illumination microscope for sample navigation, and therefore, epi-illumination micrographs provide the best reference images for general navigation. Electron microscopy can also positively identify targets for analysis, and these images are often easily comparable to the secondary electron or ion images generated during NanoSIMS analyses. Ideal mapping images range from the whole sample scale to the individual target scale, with reference points that can be used to translate from one image scale to the next.

3.3. Instrument tuning and quality control

Here, we present a brief introduction to issues that may be encountered during the tuning of a NanoSIMS 50 or 50L; more detailed instructions have been previously published (Pett-Ridge and Weber, 2012). The central aspects of SIMS instrument tuning are mass selection, resolving isobaric interferences, and peak shape:

a. *Mass selection*: To obtain accurate measurements, the secondary ion mass spectrometer must be tuned and aligned to collect ion masses of interest. Choosing masses will depend entirely upon the question being asked, what isotopically labeled compounds have been added, and whether operation is proceeding in Cs^+ or O^- mode. Often this necessitates choosing between analyzing common bioelements (e.g., C, N, O, S, P) with a Cs^+ beam or metals/metalloids (e.g., Fe, Al, Mn, Mo) with a O^- beam. If the ion yield is sufficient, some creative solutions exist, for example, Fe can be detected as FeO^- in Cs^+ mode. Alternatively, subsequent O^- mode measurement of the same spot is possible.

b. *Isobaric interferences*: When selecting ion masses, it is critical to consider and exclude isobaric interferences, which are species with near-identical masses to the species of interest. Isobaric interferences can be problematic for SIMS because the sputtering process generates molecules. Therefore, in addition to isotopes with the same mass (e.g., ^{48}Ti and ^{48}Ca), users must consider isobaric interferences that are clusters of atoms, many of which are artificial (e.g., $^{23}Na^{24}Mg^{1}H^+$). To identify potentially significant isobaric interferences, the first step is to determine the major elemental composition of the sample (here, previous SIMS studies may be helpful). Blanks and control samples can be used to determine if interfering molecules are produced at significant levels. If this turns out to be the case, the exact masses of significant isobaric interferences need to be calculated relative to the exact mass of the target species to determine difference in mass (ΔM), and the mass resolving power ($MRP = M/\Delta M$) required to resolve the target species. MRP is a metric of peak shape and the tuning of the mass spectrometer.

c. *Peak shape*: The scan of the mass peak should be both flat-topped and steep-sided. The shape of the peak is the cumulative result of everything from the primary beam location and size to the gain on the detector. A tightly focused and well-centered primary beam reduces angular aberration and minimizes potential distortions. The secondary ion beam should be aligned relative to all the lenses, slits, and apertures in the

secondary mass spectrometer in order to maximize transmission and minimize distortion. The entrance slit effectively sets the nominal MRP of the mass spectrometer, and the aperture slit and energy slit are used to steepen the peak side slopes and reach the target MRP by reducing angular and chromatic aberrations. Peak top flatness is important to measurement stability and indicates that 100% of the target species is collected to the exclusion of isobaric interferences. In addition to tuning and alignment issues, peak top flatness is also affected by the EM gain, high voltage, threshold, and deflector settings.

Standards are used during the process of setting up the mass spectrometer; they are used for mass selection, quantification, and session to session comparison of transmission, MRP, and elemental or isotopic ratios. Reference materials can be simple (e.g., iron), multielement standards like the NIST glass standard NBS610 (500 μg/g of most elements) or generated/characterized "in-house" by characterizing samples through bulk methods and verifying high-resolution homogeneity by replicate SIMS analyses. One example is the *Bacillus subtilis* spore sample used by the LLNL NanoSIMS group as a reference standard for C and N isotopic measurements ($^{13}C/^{12}C = 0.0110$; $^{15}N/^{14}N = 0.00370$). For this standard, isotopic enrichments were determined by bulk analysis at the University of Utah (Finzi-Hart et al., 2009); measurement precision, σ (internal), is ~4% (2σ) for individual $^{13}C/^{12}C$ and $^{15}N/^{15}N$. For many soil science applications, the co-occurrence of both mineral and organic phases requires that both a multielement (NBS 610) and an organic phase standard be used. However, when studying complex organo-mineral interfaces, the aim should always be to simultaneously record mineral and organic-derived ions to obtain a complete view on the studied mineral surfaces. Caution must also be exercised when applying SIMS to identify specific mineral phases. The count rate of an ion is not directly proportional to the concentration in the mineral. For example, the content of iron influences the secondary ion yield of other elements that are present in the sample. A linear interpolation based on the elemental concentration of the mineral is, therefore, not reasonable (Lehmann, 2003). It is thus advantageous to confirm mineral identity using X-ray techniques or other methods. In cases where quantification of an element is desired, mineral-specific standards are necessary.

Minerals in soil pose a particular challenge because mineral grains may accumulate an electrical charge under sustained Cs^+ primary ion beam sputtering. The phenomenon can readily be observed in the NanoSIMS

because charged regions generate very low secondary electron yields. The area of charge accumulation may still yield secondary ions, but their trajectories through the secondary mass spectrometer will deviate from those of other ions when they have significantly different energy (>10 V difference). As a result, some species may not be detected with the same relative efficiency, resulting in inaccurate measurements. This is primarily an issue for the analysis of negative secondary ions because large numbers of electrons are extracted when the sample surface is bombarded by a beam of Cs^+ ions. At the initiation of analysis, while the metal coating is still intact, charging may not be obvious. In some cases, minerals (e.g., magnetite) or organic material in the sample may provide sufficient charge conductivity to allow analysis. Most OM, while insulating in its natural state, becomes conducting under ion bombardment. However, soil particles, even those initially coated with Au, often begin to show evidence of sample charging after ~20 min of analysis, with significantly diminished total ion counts (Pett-Ridge et al., 2012). This effect has been observed in a NanoSIMS study of microaggregates deposited on silicon nitride windows, where regions free of organic material appeared to undergo the most obvious charging (Remusat et al., 2012).

The best way to overcome sample charging is to use a device called an electron flood gun, commonly referred to as the e-gun. Tuning of the e-gun requires significant experience in aligning the electrons with the primary beam on the sample and in adjusting the voltage to the charge status of the sample. Another challenge is that secondary electron imaging is not possible while the e-gun is in use. Often, it is easiest to initially locate particles of interest with secondary electron imaging and then turn on the e-gun for ion image data collection. When the e-gun is tuned correctly, nonconductive minerals will not charge and the mass peaks will maintain the same level of mass resolution as achieved on a conducting sample. We note that the sample must be covered with a conductive coating for the e-gun to work; electrons that reach the sample outside the analysis area must have a path to ground. The e-gun is not likely to work with samples with significant topography and is not a solution in cases where topography is the proximal cause of charging and ion shadowing. In tests of different mineral types performed at LLNL, using the e-gun increased the ion yield for C and N by as much as a factor of 10. Additional tests showed that isotope ratios of standard reference materials analyzed both with and without the e-gun were not significantly different (Pett-Ridge et al., 2012). Caution is always advisable when interpreting results were charging is possible.

3.4. Sample preparation—From single particles to intact soil

In the next paragraphs, we discuss possible ways to prepare soil samples ranging from primary particles and aggregates to complex intact samples containing microbial and plant tissues.

3.4.1 Direct deposition of individual particles and microaggregates

Individual soil particles (e.g., clay minerals, particulate OM) as well as microaggregates can be deposited directly onto an analysis support (e.g., Si-wafer, polished metal stubs) and imaged via NanoSIMS provided they have limited topography and remain adhered to the sample support under high vacuum.

Such materials may be derived from physical soil fractionation (Eusterhues et al., 2005) or taken directly from a soil suspension (Keiluweit et al., 2012). The application of ultrasound during soil fractionation may destroy natural soil structure and also redistribute both organic compounds and individual mineral particles between physical fractions (Amelung and Zech, 1999; Mueller et al., 2012a). While pretreatments needed to isolate small particles may introduce experimental bias, it may still be desirable to attempt direct observations of small particles or microaggregates, especially when the nature of the research question prohibits the use of C- and N-containing fixatives. Samples can be deposited on flat surfaces such as polished metal stubs, Si-wafers, gold foil, or directly on SEM or TEM grids (Keiluweit et al., 2012; Mueller et al., 2012b). Alternatively, particles can be collected from soil suspensions on gold-coated filter discs, a widely used preparation technique in microbiology (Musat et al., 2012). For obvious reasons, the sample support must be chosen with the elements of interest in mind (Si-wafers are not advisable when Si is a target element). In the direct deposition preparation technique, a single layer of small particles/microaggregates should be deposited on the sample support to minimize topography. If the goal is to simultaneously explore both mineral and microbial constituents, fixation of the biological tissues will be necessary (see below for detailed description).

3.4.2 Fixation and preparation of organic materials

A variety of biological sample types may be of interest to soil scientists, ranging from root or hyphal tissues to bacterial and archaeal cells, protists and microfauna, or decaying plant litter. For all these sample types, preservation of cell structure is important for target identification and to contain mobile organic and inorganic constituents. Sample preparation typically involves

stabilization of biological components (fixation), removal of water (dehydration) and salts (derived from growth media or sea/soil water), deposition of the sample on a conductive support (Si-wafer, TEM grid), and subsequent whole cell analysis or thin sectioning after embedding. Fixation of biological tissues is a process used to preserve cell morphology from decay and immobilize analytes of interest by increasing molecular mechanical strength or stability. Chemical fixation for imaging analysis is typically performed with aldehydes (e.g., glutaraldehyde, paraformaldehyde, formaldehyde) that cross-link proteins to hold cell structure together during dehydration, (Kuo, 2007; Nunan et al., 2001; Tippkötter and Ritz, 1996). Low-temperature methods like flash freezing and high-pressure freezing (Chandra and Morrison, 1992; Dykstra and Reuss, 2003; Echlin, 1992) are an alternative in some circumstances if it is critical to preserve the distribution of small molecules and diffusible ions. For biological samples that are to be analyzed intact, collection on a filter is very efficient, and nucleopore or polycarbonate filters can be used as a sample support for SIMS analysis if they are kept flat at the micron scale. Samples grown on a solid sample support can be immersed in fixative and gently washed by repeated immersion in deionized water.

If subcellular elemental or isotopic distributions are of interest in soil microbial or plant tissue samples, fixation is often followed by embedding (impregnating the sample with a hard, vacuum stable matrix) and sectioning (cutting the sample into cross sections) prior to NanoSIMS analysis. Samples can be embedded in a number of polymers for room temperature sectioning (e.g., epoxy, acrylic, paraffin (Dykstra and Reuss, 2003)). Cryogenic sectioning can be performed with sucrose, OCT, or similar compounds. Cryosectioning of frozen (water/ice embedded) samples is also an option but is more technically challenging and requires much practice. Sectioning can be performed with an ultramicrotome, a standard histological microtome or cryostat, or even with a razor blade, depending on the type of pre-NanoSIMS imaging that is desired. An adhesive surface coating (e.g., poly-L-lysine, vector bond, egg white) can be used to retain sections during washing or staining. Such surface coatings can also be used for the fixation of other thin sections or microscale single particles on sample mounts (e.g., Me-stubs, Si-wafers). Contrast stains used for TEM imaging of biological ultrastructure (e.g., uranyl acetate) typically are compatible with SIMS because mass spectrometry can easily resolve the stain components from many species of interest. However, there may be cases where contrast stains would be a source of unwanted background counts, particularly for metal

analysis. Standard TEM-grade ultrathin sections (~100 nm) can be analyzed by high-resolution NanoSIMS, but with a limited analysis time to avoid section breakage or consumption. To extend the SIMS analysis time and collect more data while still allowing correlated TEM–SIMS analysis, thicker sections (up to 500 nm) can be prepared, though with a loss in TEM image quality. Thicker sections are also desirable if large areas (mm^2) need to be analyzed. Focused ion beam (FIB) milling can also be used as an alternative to embedding and sectioning (Weber et al., 2010), particularly where the user needs to have precise control over the location and orientation of the sample thin section. Thin sections can be laid on a TEM grid or directly on a solid substrate prior to SIMS analysis. For example, this technique was used by Bonneville et al. (2011) to prepare cross sections of a microscale fungal hyphae/biotite interface for subsequent TEM analyzes. If transmission light imaging is necessary for sample mapping, indium tin oxide (ITO)-coated glass slides are preferable to uncoated glass slides because the ITO coating does not charge under ion bombardment.

3.4.3 Preparation of aggregated soil structure and intact plant–soil systems

Many soil researchers would like to be able to image cross sections of both biological and mineral phases in intact plant–soil samples. However, three-dimensional multiphase objects often require additional preparation steps that go beyond what is required for a purely organic or purely mineral sample. Essentially, the object of interest needs to be embedded in a solid, vacuum-compatible medium and subsequently cut and or polished to generate a flat surface. The primary distinction between preparation of organic materials (see above) and preparing soil samples is that cutting heterogeneous samples must accommodate both "hard" (quartz, Fe oxides) and "soft" components (plant tissues).

The most useful approaches for NanoSIMS soil sample preparation fall into three general categories: (1) embedding with resin (epoxy, acrylic, polyester), sucrose, or paraffin; (2) embedding in molten elemental sulfur (S); or (3) cryotechniques. The appropriateness of these three techniques depends on the target elements which are to be analyzed and the size of the sample (microaggregate vs. intact soil core). In general, resin embedding is the most useful approach for larger aggregates and soil cores, whereas cryopreservation/sectioning and S embedding are the best choices for small (~100 μm) microaggregates. Cryo and S embedding have the added benefit that no artificial C or N is added as background material. We note that it may be

possible to subtract a background resin signal from the sample signal using the difference in the CN-/C-ratio, (e.g., the biological from the non-biological material). The CN-/C-ratio of resin is quite distinct from that of biological material, so regions representing resin within analysis images can be omitted at the data processing stage (Weber et al., 2012).

For larger specimens such as macroaggregates (>2 mm) or intact soil cores containing both hard mineral constituents and soft tissues such as plant residues (e.g., roots in Fig. 1.5), microbes, and plant roots, resin-embedded sections are typically created and then polished for further analyses. One epoxy resin approach was described by Herrmann et al. (2007a), who developed a technique for the preservation of microbial communities in quartz-based soils that was later modified by Clode et al. (2009) to include plant roots. Infiltration of samples in acetone–epoxy resin mixtures was conducted over a period of days, with the concentration of "Araldite" (epoxy resin) gradually increased until 100%. At a larger spatial scale, at TU München, this procedure was successfully applied to prepare natural intact soil cores for

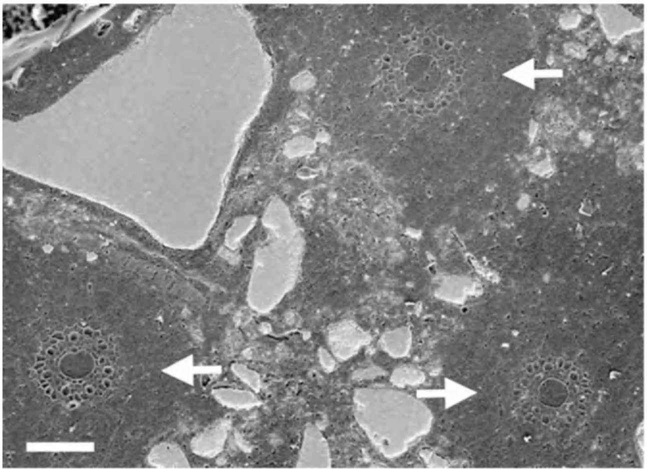

Figure 1.5 SEM micrograph (figure 1 adapted from Clode et al., 2009) of three roots (*Triticum aestivum*) in soil, showing harder materials as quartz (light areas) and softer materials including roots (dark gray areas). The loamy sand textured soil (Ap horizon from Meckering, Western Australia) containing the roots was infiltrated in acetone araldite mixtures over several days, using a gradually increasing araldite concentration. Final embedding in Araldite 502 was done according to Herrmann et al. (2007a). Embedded samples were cut in slices, reembedded in 10 mm mounts, and polished using silicon carbide paper and finally diamond paste. *Republished with permission of American Society of Biologists (www.plantphysiology.org), from Clode et al. (2009), Copyright 2012, permission conveyed through Copyright Clearance Center, Inc.*

NanoSIMS analyses from the permafrost layer of cryoturbated soils (see Fig. 1.2). Previous studies show that the abundance of nitrogenous compounds was not adversely affected by this procedure (Herrmann et al., 2007a; Peteranderl and Lechene, 2004).

An alternative to resin embedding is sulfur embedding (De Gregorio et al., 2010; Flynn et al., 2004; Lehmann et al., 2005) which has been successfully used to section heterogeneous soil aggregates (Herrmann et al., 2007a; Lehmann et al., 2005). The most significant benefit of S embedding is that aggregates can be embedded in a non-C-based, room temperature sectionable medium. In the De Gregorio et al. (2010) approach, elemental sulfur is heated to its molten state (>100 °C) and then a soil aggregate is inserted and allowed to cool. The resulting material can be glued to a metal stub and sectioned using an ultramicrotome. Unfortunately, the sulfur may provide only limited structural integrity for the sections because it tends not to impregnate samples extensively. Also, the high temperature could potentially alter organic materials, particularly those on the surface of the aggregate. A low-temperature alternative, the S embedding approach described by Lehmann et al. (2005) consists of S heated until molten and rapidly cooled in liquid N_2. As the S is slowly warmed to room temperature, it goes through a phase of high viscosity and at this stage (~20 s) aggregates may be inserted into the S. The resulting S block remains amorphous or plastic for a limited amount of time, during which sectioning should be carried out.

A final option for fixation and sectioning is the cryopreservation/sectioning approach used by researchers at LLNL: high-pressure freezing (Leica EMPACT2) of soil aggregates surrounded by ultrapure H_2O in small copper tubes (16.6 mm) with an internal diameter of 350 μm, followed by cryosectioning and freeze drying. This approach results in samples of regular thickness (<400 nm) and minimal chemical changes (Fig. 1.6). This method, though challenging, preserves the distribution of diffusible ions and molecules. Because it involves fast freezing but no cyroprotectant, no background material is introduced that might dilute the C or N isotopic signal (Fig. 1.6).

Once a soil sample is embedded, it must then be cut to expose a cross section for NanoSIMS analysis. The presence of mineral grains significantly increases the difficulty of sectioning samples. While ultramicrotomy with a diamond knife is possible, it is significantly easier to cut embedded soil aggregates and cores with a wafer saw and then polish them as per a geological sample. This is, however, not ideal for some softer biological materials

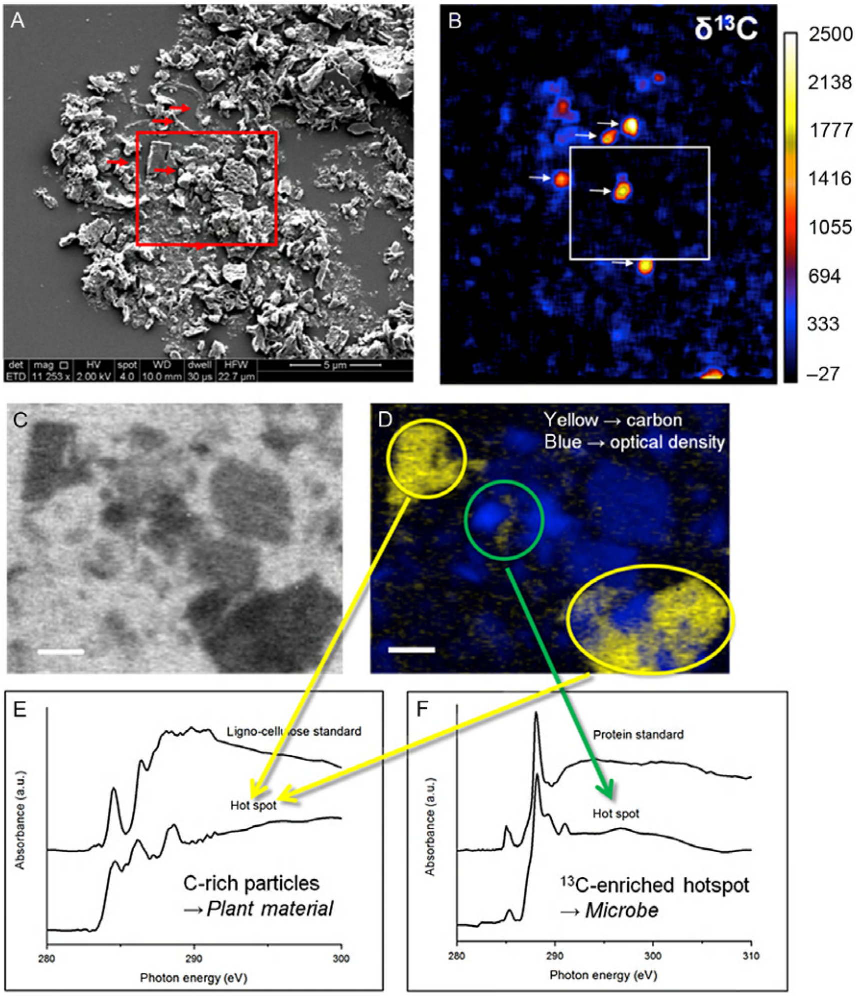

Figure 1.6 A soil thin section prepared by "cryo"techniques: high-pressure freezing followed by cryosectioning and then freeze drying. The soil is from a clay-rich forest soil from the H.J. Andrews Experiment Station, Oregon, USA and was exposed in a controlled microcosm to a low concentration ^{13}C glucose label. (A) SEM micrograph collected at 2 kV, (B) NanoSIMS $\delta^{13}C$ image showing what appear to be isotopically enriched microbial cells (white arrows) flanked by plant residue particles, (C) STXM transmission image collected at 300 eV of the region annotated by the red/white box in (A) and (B), scale = 1 µm; (D) false color overlay of a STXM C difference map (ratio of scans collected above and below the C edge) and the transmission map shown in (C); (E and F) NEXAFS spectra extracted from the regions of interest circled in (D) are plotted against the standard spectra for (E) ligno-cellulose and (F) protein and substantiate plant versus microbe particle definitions. *M. Keiluweit, J. Bougoure, P. Weber, P. Nico, M. Kleber, J. Pett-Ridge (unpublished data).*

and resins, which can abrade more easily, resulting in topographical differences across the sample surface. This abrasion effect can be particularly pronounced at the edges of mineral grains, where inorganic–organic interfaces are located.

Sectioning via ultramicrotomy is the primary alternative option to saw cutting and has proven highly effective for combined TEM and NanoSIMS stable isotope measurements of plant–soil systems (Clode et al., 2009). In Fig. 1.5, a SEM image of three embedded roots illustrates how the heterogeneous distribution of soft and hard soil compartments can both be preserved in a thin section (Clode et al., 2009). In this procedure, both plant tissues and microorganisms appeared to be well preserved (Figs. 1.4 and 1.5). We note that the sectioning of embedded soil aggregates with heterogeneous density requires a highly skilled operator; it is easy to chip a diamond knife. A final option for sectioning fixed samples is FIB sectioning. This approach is a particularly good option for preserving the distribution of diffusible species because a fully dry sample can be sectioned; however, the method requires specialized equipment and limited sample material can be processed. If the samples are only destined for SIMS analysis, top cutting is a more rapid FIB option (Weber et al., 2010).

3.5. Data acquisition and analysis

There are two main data collection modes possible with the NanoSIMS 50: spot measurements and ion images. The collection of secondary ions in the spot mode is usually used for the direct recording of isotopic ratio data for a discrete location. However, the main data collection mode for soil-related studies is likely to be ion imaging because users working with highly complex samples are usually interested in spatially explicit isotope ratios and contextual information. NanoSIMS ion image files consist of individual images for each scan (plane) for each given mass, along with metadata describing the conditions of the analysis. There are a number of image processing software options available to analyze the ion image data. WinImage is Cameca's Windows-based image processing package that comes preinstalled with the Windows-based NanoSIMS software. The previous Solaris-based NanoSIMS software featured a somewhat rudimentary ion image processing application called simply, Image. Another software package for SIMS image processing is the Windows-based LIMAGE program developed by Larry Nittler at the Carnegie Institution of Washington (independent from Cameca). In addition to these commercial programs, there are two open source packages. The National Resource for Imaging Mass Spectrometry

group at Harvard University has developed a plugin for the Java-based freeware ImageJ. The so-called MIMS plugin provides a number of specific data processing options in addition to the full range of ImageJ capabilities. Most notable is the ability to express ratio images on a Hue–Saturation–Intensity scale, where the scale parameters can be set by the user. Finally, a very recently developed software is the Matlab-based application Look@NanoSIMS developed by Lubos Polerecky at the Max-Planck Institute for Marine Microbiology in Bremen (Polerecky et al., 2012). No matter what software is used, there are some basic steps for the processing of NanoSIMS images (the sequence of steps may vary slightly for some specific data sets or research questions).

Briefly, the first step of image analysis is to examine all obtained images for possible flaws (e.g., spots of charging, unrecorded spots, or lines within images). When multiple cycles are recorded, the analyst has to decide whether any cycles should be excluded from further analysis. Individual cycles should be aligned to correct for primary beam drift and also dead-time corrected. This dead time is the period when the detector has counted a single secondary ion but is not ready to count another (usually tens of nanoseconds). Next, the species of interest are normalized to major element species (e.g., $^{13}C^{-}/^{12}C^{-}$ or $^{12}C^{-}/^{12}C^{14}N^{-}$); ratio images can be used efficiently to evaluate the quality of the ratio data and the distribution of normalized data. Typically, quantitative data are obtained by defining ROIs, which consist of a group of pixels bounding a particular feature. In most image processing applications, an ROI can be drawn directly onto the image, and the software then records the sum of the counts from the pixels within the ROI and thus also ratio data. Defining ROIs is a critical step. Without objective criteria, it is possible to change the isotopic enrichments just by changing the size of an ROI. The best ROI selection criteria are external images (e.g., SEM image or fluorescence image) or single ion images (e.g., $^{56}Fe^{16}O^{-}$ for iron oxide particles). Alignment with an external image is possible when using the Look@NanoSIMS software. In many cases, it is necessary to visually evaluate the spatial distribution of several ions to interpret and properly define ROIs. Unfortunately, there are no standard procedures for feature selection in complex matrices like soils.

After ROIs are defined, the data can be extracted and interpreted. One promising way to evaluate microscale ion images might be use of geostatistics, which are often used for larger plot or ecosystem analyses (Steffens et al., 2008). Geostatistics can be used to identify dependencies within any spatial data (e.g., NanoSIMS ion images). For example, it might

be possible to use this approach to evaluate the spatial distribution of Fe within a complex soil matrix. Figure 1.7 illustrates the application of a statistical approach (R 2.13.1, R Development Core Team, 2011) in combination with the g-stat 2.4.0 package (Pebesma, 2004) to evaluate spatial dependencies between OM ($^{12}C^{14}N^{-}$) and particles containing iron ($^{56}Fe^{16}O$). The analysis is based on data extracted from a 32-μm line scan drawn on the NanoSIMS images (Fig. 1.7A and B). The sample is a Cambisol soil aggregate embedded in Araldite, originally from Höglwald, Bavaria, Germany. Both semivariograms for $^{12}C^{14}N^{-}$ and $^{56}Fe^{16}O^{-}$

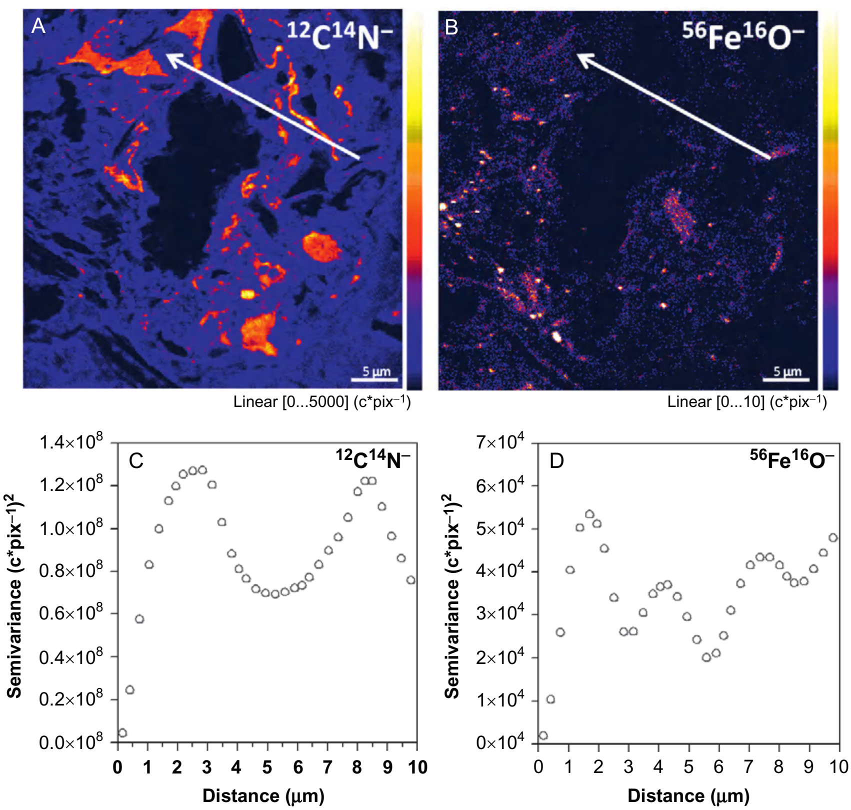

Figure 1.7 NanoSIMS images and semivariograms (lower panel) of an embedded cross section of organic matter derived from a aggregate of Cambisol topsoil (Ah horizon) from Höglwald, Bavaria, Germany. (A) NanoSIMS $^{12}C^{14}N^{-}$ ion image, (B) NanoSIMS $^{56}Fe^{16}O^{-}$ ion image. The white arrow in the NanoSIMS images indicates the line scan which was used to generate the semivariograms in (C) and (D). *C. W. Mueller (unpublished data).*

(Fig. 1.7C and D) show a comparable periodic behavior, where the semivariance is oscillating (*y*-axis). The semivariance is a measure of spatial dissimilarity. Thus, the wave-like appearance of the semivariance demonstrates a distinct spatial pattern of similar ion counts ($^{12}C^{14}N^{-}$ and $^{56}Fe^{16}O^{-}$) and thus a regularity in the aggregate architecture (organic and mineral spheres). But as the spatial frequency (*x*-axis) of the maxima and minima of the semivariance is different between $^{12}C^{14}N^{-}$ and $^{56}Fe^{16}O^{-}$, this indicates differences in spatial structures and different pattern sizes. This analysis indicated that iron clusters ($^{56}Fe^{16}O^{-}$) are spatially independent from OM ($^{12}C^{14}N^{-}$). Similar analyses may be particularly useful to reveal spatial interdependencies between mineral and organic soil constituents or even between areas enriched or depleted in specific stable isotopes. Another approach to NanoSIMS data analysis is the upscaling approach used by Fike et al. (2008). They collected numerous single spot (6 μm × 6 μm) NanoSIMS measurements (>300) and measured the isotopic variability of sulfide within the oxycline of a cyanobacterial mat (sampling grids: 3500 μm × 450 μm and 3000 μm × 500 μm, spatial increment of 50–200 μm). Analyzing the $\delta^{34}S$ abundance and isotopic fractionation, they observed fine-scale laminations (1–400 μm) and clear zonation. This work suggests that single spot NanoSIMS measurements, collected on up to a millimeter scale and linearly interpolated, could be applied for upscaling micrometer spot data in soils.

4. COMBINATION WITH OTHER MICROSCALE TECHNIQUES

4.1. Scanning and transmission electron microscopy

Prior to the development of NanoSIMS, electron microscopy was the approach of choice for the observation of soil particle arrangements (Gillott, 1970; Gray, 1967; Howard et al., 1996; Kowalkowski and Mycielskadowgiallo, 1985). Electron microscopy has evolved to achieve very high resolution, touching on 1 nm in SEM and 0.05 nm in TEM. Similar to NanoSIMS, electron microscopy techniques can be used to obtain information about the material properties of a sample, in addition to providing an image. In a SEM, a high-energy focused beam of electrons is produced. The electrons interact with electrons in the sample, producing secondary electrons, backscattered electrons (BSEs), and characteristic X-rays (energy-dispersive X-ray spectroscopy (EDX/EDS/EDXS)) that can be detected and that deliver information about the sample's surface topography and composition. An SEM–BSE image is a good tool to

differentiate between organic and mineral spheres. This can be useful in samples without topography such as polished soil cross sections. The crystalline state of a sample can be determined by recording patterns of the diffracted backscattered electrons (EBSD) and matching them with a data base for crystallographic structures. An EDX scan yields information on the localization of minerals versus OM and is useful for identifying ROIs within the sample.

It should be noted, however, that in contrast to NanoSIMS, where information is gathered only from secondary ions sputtered from the uppermost atomic layers, the interaction volume of secondary ions in SEM extends in a pear-shaped fashion between 100 nm and 5 μm deep into the sample (depending on the energy of the electron beam, atomic number, and density of the specimen). EDX is therefore not a surface technique *sensu strictu*, and it has been shown that TEM maps do not always compare well with subsequently obtained NanoSIMS images (Badro et al., 2007).

4.2. Synchrotron-based techniques

To study soil process dynamics as a function of location within aggregates and microaggregates, simultaneous information on (a) localization, (b) identification, and (c) transformation of OM and mineral phases is required with very high spatial resolution. Conventional electron microscopes can visualize basic elemental composition but are unable to speciate carbon compounds. A number of techniques can yield data on C composition (ion microprobe laser desorption, laser ionization mass spectrometry, Raman microscopy, ^{13}C NMR, FTIR (Lehmann et al., 2005, 2009)), though few can provide molecular or elemental characterization with the submicron resolution necessary to study mineral–organic interactions in microaggregates. These goals can be approximated with the combination of NanoSIMS and STXM/NEXAFS. The resolution of synchrotron-based X-ray microscopes can approach 50 nm, comparable to the NanoSIMS spot size. This soft X-ray technique allows to collect raster scan images across energy ranges corresponding to a variety of suitable elemental core edges (e.g., carbon, calcium, nitrogen, oxygen, and iron). The spatially resolved NEXAFS spectra extracted from the respective image "stacks" reveal the bonding environment of the element of interest, allowing the speciation of OM forms and elemental redox states. STXM/NEXAFS has been used successfully to describe spatial patterns and speciation of SOM-associated carbon (Kinyangi et al., 2006; Lehmann et al., 2005, 2007; Schumacher et al., 2005; Wan et al., 2007a) and nitrogen in a broad range of environments, including marine systems (Brandes et al., 2004).

A combined "STXM–SIMS" approach allows precise, quantitative measurement of molecular and isotopic patterns in undisturbed samples, at high resolution (Keiluweit et al., 2012; Pett-Ridge et al., 2012). By combining NanoSIMS with STXM/NEXAFS, it is possible to map organic C distribution, to image associations of organics with specific mineral types, and to trace OM of variable origin into the soil matrix (Lehmann et al., 2007; Wan et al., 2007b). If combined with isotope tracer experiments, the images acquired through this approach can document the forms of C that become stored in soil aggregates and simultaneously track microbial debris and other organic polymers into the soil matrix.

Technical challenges to the combined application of STXM and NanoSIMS have recently been summarized by Pett-Ridge et al. (2012). They point out that experimental activities have to be planned in a way such that STXM analysis precedes NanoSIMS, as the latter method has a much greater potential for destructive interference with the sample. Sample holders commonly used in synchrotron spectroscopy may contain N (Si_3N_4) or C (TEM Cu grids with C lacey) and must therefore be chosen to avoid unwanted secondary ion species (e.g., $^{12}C^-$, $^{12}C^{14}N^-$) in subsequent NanoSIMS applications. For STXM/NEXAFS analysis, samples need to be thin enough to allow for X-ray transmission ($\sim$200–600 nm). This limits the type of microstructures that can be observed with both methods at the same time to thin platelet-like objects. Taking these restrictions into account, SEM, NanoSIMS, and STXM may be applied to the identical soil sample specimen, providing information that is complementary: SEM may be used to generate a mesoscale surface image of ROI, STXM/NEXAFS imaging can obtain information about whole sample chemistry, and NanoSIMS analysis can yield elemental/isotopic data either on surface characteristics or from a depth profile (Pett-Ridge et al., 2012) (Figs. 1.6 and 1.8). To allow for high-resolution SIMS imaging and STXM/NEXAFS spectromicroscopic analysis of the same sample, a specimen must be prepared with limited topography, able to withstand high vacuum, dry, conductive, thin enough to allow photon transmission, and prepared without carbon-based reagents.

An example for the synergistic application of NanoSIMS and STXM/NEXAFS was recently presented by Keiluweit et al. (2012). These authors employed NanoSIMS to follow the fate of isotopically labeled amino sugars from fungal cell walls as they became metabolized or bound to minerals and SOM. Concurrently, STXM/NEXAFS spectromicroscopy was used to determine the chemical transformations of substrate C and N functionalities during the process (Fig. 1.8). The authors determined that ^{15}N-labeled amide

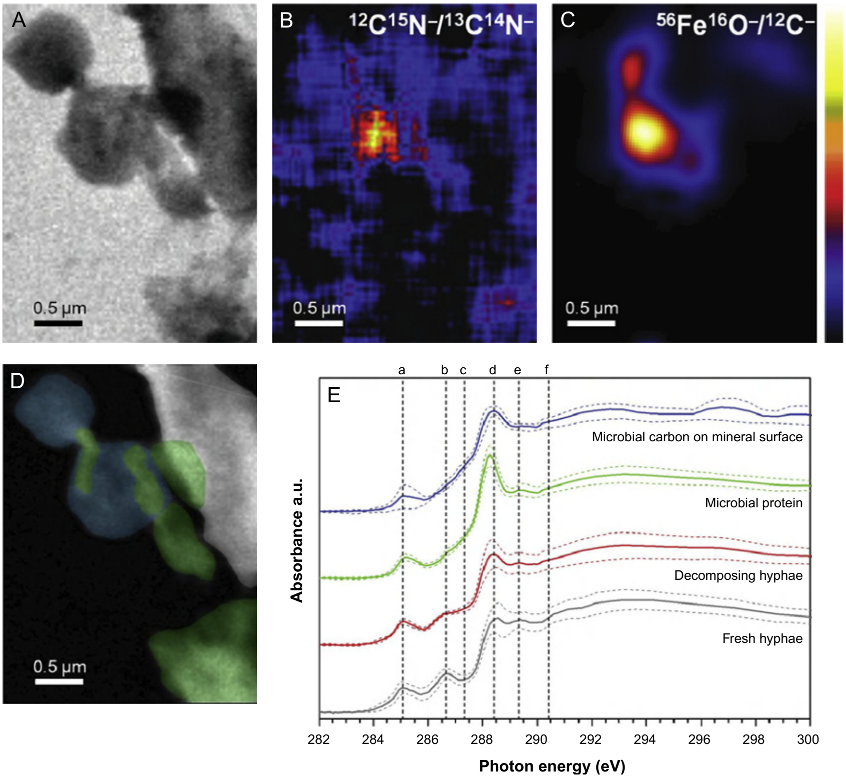

Figure 1.8 Microstructures associated with fungal hyphae in an organic forest soil investigated by both NanoSIMS imaging and STXM/NEXAFS spectromicroscopy. (A) STXM optical density map recorded at 300 eV; (B and C) NanoSIMS isotope ratio images for $^{12}C^{15}N^-/^{13}C^{14}N^-$ and Fe concentrations ($^{56}Fe^{16}O^-/^{12}C^-$, normalized to carbon) of the same feature shown in the STXM image. Brighter colors reflect high enrichment/concentration. (D) Optical density map of hyphal-associated microstructures with colored regions of interest (ROIs) from which NEXAFS spectra at the C 1s absorption edge and the N 1s absorption edge were collected. ROIs are color-coded according to the spectral types extracted from them: intact fungal hyphae (gray), decomposing hyphal residue (brown), microbial residue (green), and mineral surfaces (blue). (E) Average NEXAFS spectra representing the major carbon forms encountered in the regions of interest defined in (D). Carbon 1s absorption edge peaks are identified as C=C 1s–π^* transition of aromatic C at 285.1 eV (a), 1s–π^* transition of C=C in ene-ketone at 286.7 eV (b), 1s–3p/σ^* transition of aliphatic C at 287.4 eV (c), 1s–π^* transition of carboxylic and/or amide C at 288.3 eV (d), the 1s–3p/σ^* transition of alcohol C—OH at 289.4 eV (e), and the 1s–π^* transition of carbonyl C at 290.3 eV (f). *Adapted from Keiluweit et al. (2012), Copyright (2012), with permission from Elsevier.*

N derived from fungal cell wall material preferentially associated with Fe (hydr)oxide surfaces or Fe–OM coprecipitates on the surface of other minerals. Through the combination of NanoSIMS and STXM/NEXAFS, it was further possible to determine that amide N found on mineral surfaces originated from bacterial protein rather than from the original amino sugars or from nucleotides. This example illustrates that combined applications of synergistic imaging techniques such as NanoSIMS and STXM have the potential to provide information about OM–mineral–microbial relationships while avoiding the artifacts inevitably generated by chemical or physical fractionation procedures.

4.3. Atomic force microscopy

The AFM is another tool for imaging, measuring, and manipulating matter at the nanoscale. An AFM consists of a cantilever with a sharp tip that is used to scan the specimen surface. When the tip is brought into proximity of a sample surface, forces between the tip and the sample lead to a deflection of the cantilever. The deflection of the cantilever is measured and converted to an image of the sample surface. Reports on AFM applications in soil science are increasing (Cheng et al., 2008; Rennert et al., 2012; Schaumann and Mouvenchery, 2012; Totsche et al., 2010) and typically provide information about local topography and properties of minerals and soil aggregates surfaces at very high spatial resolution. To date, the focus of soil-related AFM work has been on interactions between microorganisms and minerals, mainly iron oxides and hydroxides (Maurice, 1996; Maurice et al., 2000). Balogh-Brunstad et al. (2008) combined SEM and AFM to investigate fungal weathering of biotite in a batch liquid culture.

One potential combined AFM–NanoSIMS application could be the use of AFM to correct for topography effects in NanoSIMS analyses. Here, AFM would be applied both before and after SIMS, allowing the user to convert SIMS data into a true three-dimensional representation of the analyzed species (Fleming et al., 2011). Wirtz et al. (2012a,b) report the development of an integrated SIMS–scanning probe microscope (SPM). In this instrument, a specially developed SPM system was integrated in a Cameca NanoSIMS 50, allowing the user to record topographical *in situ* images of the sample surface before, in between, and after SIMS analysis.

4.4. *In situ* single-cell labeling

Environmental microbiologists see particular value in the combination of *in situ* phylogenetic labeling and NanoSIMS in order to link metabolic

function with taxonomic identity (Kuypers and Jorgensen, 2007). This capacity was first demonstrated using a combination of conventional SIMS and FISH to analyze an archaeal–bacterial consortium in anoxic marine sediments (Orphan et al., 2001). The FISH–SIMS combination allowed Orphan et al. (2001) to demonstrate that cell aggregates binding a specific archaeal probe were strongly depleted in ^{13}C, indicating a methane-based metabolism. In many natural microbial systems, this approach may be even better suited to NanoSIMS, as it can provide this information at the length scale of an individual bacterium (~1 μm). Two variations of this approach are currently used: element-labeled FISH (EL-FISH) where catalyzed reporter deposition FISH (CARD-FISH) is used to deposit high concentrations of fluorine-containing fluorophores in target cells (Behrens et al., 2008); or halogen-labeled *in situ* hybridization where a standard FISH protocol is used in combination with halogen (I, Br)-tagged probes (Li et al., 2008). NanoSIMS can then be used to visualize the labeled cells by acquiring a signal for ^{19}F, which is not naturally present at high concentrations in most environmental cells (Behrens et al., 2008; Halm et al., 2009; Musat et al., 2008). In these approaches, a phylogenetic probe is linked to a highly electronegative elemental label (fluorine, iodine, gold, selenium, or bromine) instead of the typical fluorophore, which can be detected in concert with ^{13}C and ^{15}N isotopes for functional characterization. These approaches enable simultaneous localization of the tag and chemical mapping in the NanoSIMS. It may even be possible to use FISH-SIMS approaches in embedded samples (Woebken et al., 2012). The work of Lemaire et al. (2008), where fixed samples were embedded in TissueTek® (Sakura Finetek Labware & Accessories) and then cryosectioned and FISH-labeled, suggests that this may be possible. However, its usefulness in soil may be limited unless a means to overcome soil's natural background fluorescence is developed. Also, care must be taken with quantitative interpretation of FISH–SIMS results, since these approaches may reduce the original cell enrichment by 60–80% for ^{13}C and 30–60% for ^{15}N (J. Pett-Ridge and S. Behrens, unpublished data).

5. CONCLUSION

Over the last decades, soil scientists have gained a working knowledge of fundamental soil processes ranging from the stabilization of OM to microbial diversity in soils. We are now able to track the fate of specific molecular biomarkers into organo-mineral associations and to determine the microbial communities responsible for the turnover of specific organic compounds.

However, commonly used bulk analyses average over a vast swath of microbial and mineral landscapes and can miss microscale phenomena caused by specific microhabitats or distinct spatial heterogeneities in the formation of organo-mineral assemblages or soil aggregates. Thus, while our knowledge of bulk scale biogeochemical soil processes is expanding, we have lacked the high-resolution techniques needed to illustrate the mechanistic underpinnings of such processes in intact soil structures.

The emerging class of nano- and microscale spectroscopic and spectrometric techniques opens a new avenue for the fundamental understanding of soil processes. Though the first review of NanoSIMS in soil ecology by Herrmann and colleagues was in 2007 (Herrmann et al., 2007b), this field is still in its early phase. But a growing number of soil scientists successfully implement nano- and microscale spectroscopy and spectrometry in their experimental concepts, achieving a continuous progress in solving technical and experimental challenges. However, for a complete understanding of soil microscale processes, it will be crucial to combine different experimental and methodological approaches ranging from microbiology to plant/root physiology and biogeochemistry. Looking forward, the main challenge will be the upscaling from microscale analyses to individual soil horizons and the pedon or even to complete ecosystems. These improvements may not come soon, but the ability to map elements and stable isotopes at a previously unresolved spatial scale permits the combination of established isotopic enrichment techniques with the description of their spatial distribution in soil microenvironments. The application of NanoSIMS in soil science will shed a fundamentally new light on soil processes, one that is rooted at the relevant scale of microbial, mineral, and OM interactions.

ACKNOWLEDGMENTS

The authors thank H. Lugmeier, M. Hanzlik, M. Keiluweit, J. Bougoure, and P. Nico for their help and support with imaging. The oak clones were cultivated by the group of F. Buscot at the UFZ in Halle, Germany. The oak root experiment was carried out together with T. Grams and O. Angay, and the samples were prepared by M. Greiner. The sampling campaign of the Alaskan samples was funded by the NSF Postdoctoral Fellowship in Polar Regions Research (#0852036) and the DFG "Initiation of International Cooperations" (MU 3021/2-1). We thank J. Kao-Kniffin, J. Bockheim, and K. Hinkel for their help with sampling and sample preparation of the Alaskan samples. We thank M. Steffens for his assistance in geostatistics. The NanoSIMS instrument at TUM was funded by DFG (KO 1035/38-1). We acknowledge financial support from the Distributed Infrastructure for Experimentation in Ecosystem Research (EXPEER) under FP7 -262060. Work of P. K. W. and J. P.-R. was performed under the auspices of the United States. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344, with funding provided by an LDRD "Microbes and Minerals: Imaging C Stabilization" at LLNL to J. P.-R and P. K. W.

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CHAPTER TWO

Conservation Practices for Climate Change Adaptation

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Contents

Abstract

The threat of climate change is a great challenge to sustainable land management (USDA-NRCS, 2010a). Several publications have reported that over the last few decades, rainfall intensities have increased in many parts of the world, including in the United States. Without good, productive soils and the ecosystem services provided by them, the survival of our species will be in jeopardy. The future changes in climate that will drive erosion processes will significantly impact soil erosion rates, with higher

Advances in Agronomy, Volume 121
ISSN 0065-2113
http://dx.doi.org/10.1016/B978-0-12-407685-3.00002-5

projected erosion rates for the United States. These higher erosion rates will significantly contribute to lower soil productivity, lower soil organic matter content, lower soil quality, and higher rates of nutrient loss that will contribute to a reduction in the inherent soil fertility that is so important for maintaining viable economic systems and sustainability. These same hydrological changes will also include the occurrence of occasional droughts, and for some regions, such as the southwestern United States, projections suggest that there will be a decrease in precipitation and a drier region, which will have negative effects on plant productivity and increase the potential for wind erosion.

Farmer management adaptations and use of conservation practices to adapt to a changing climate (e.g., no-till practices, crop rotations, precision conservation, crop selection and dates of planting, harvest, and tillage) have the potential to greatly reduce soil erosion rates. Conservation practices will be key and must be used as strategies for adaptation to climate change impacts on the soil resource. Examples of key strategies are the use of conservation tillage, management of crop rotations and crop residue (including use of cover crops where viable), management of livestock grazing intensities, improved management of irrigation systems, use of technologies, and precision conservation. Many other conservation practices also have the potential to reduce much or all of the potential acceleration of soil erosion rates that may occur under a change in climate that will bring more total rainfall with higher intensity rainfall events, or a change to a drier climate that will potentially bring higher wind erosion rates. One important adaptation practice will be to consider projected spatial changes in the hydrological cycle, such as wetter and drier regions, and periods of drought. This could help in the development and/or implementation of soil and water conservation policies that consider temporal and spatial effects from climate change at the regional level. These policies should also consider conservation practices that contribute to increased water-holding capacity in the soil profile, improved drainage practices, and the development of new crop varieties and cropping systems that are more resistant to drought.

1. AGGREGATE IMPACTS

Agriculture is directly impacted by climatic variables of temperature, precipitation, solar radiation, and atmospheric composition that can affect plant growth and yield responses. Plant growth responses and yields are also linked closely to soil and water resources, which are similarly closely linked to climate. The interdependencies between agriculture, climate, and soil and water resources contribute to create a complex system that can respond to, and is sensitive to, changes in climate. Due to this close linkage between soil and water resources and agriculture, the effects of climate change on agriculture are one of the aggregated impacts that transcend the impacts on any one individual component of this complex system. Changes in precipitation, for example, influence the potential of water availability, but the

actual amount of available water for crops depends on several factors such as surface water runoff, crop residue at the surface, soil texture, soil water-holding capacity, infiltration rate, and other factors. Thus, the impact of climate change on all these factors will generate aggregate effects due to a change in precipitation that are not determined only by the change in precipitation amount. It is also important to understand the potential positive effects of conservation practices to mitigate and adapt to climate change (Delgado et al., 2011), as well as how we manage agricultural systems (Lal et al., 2011).

2. POTENTIAL EFFECTS OF CLIMATE CHANGE ON SOIL RESOURCES

Climate change presents a major challenge to sustainable land management (USDA-NRCS, 2010a). The effects of climate change on soil and water resources on agricultural land are critical and must be addressed with U.S. conservation policy and practice. The magnitudes and extent of increased rates of soil erosion and runoff that could occur under simulated future precipitation regimes are large, and analyses of the climate record in the United States have shown that changes in precipitation have already occurred across the country, with large observed trends in precipitation and the bias toward more extreme precipitation events (Groisman et al., 2005). Increases in soil erosion and runoff from cropland have the potential to reverse much of the past progress that has been made in reducing soil degradation and water pollution from cropland in the United States. In the arid and semiarid rangelands of the western United States, there is concern that increased periods of drought accompanying a drier environment can change ecosystem composition and reduce vegetative cover that protects the soil from both wind and water erosion. Since soil degradation is closely related to soil erosion, there can be a negative impact on soil quality, productivity, and associated ecosystem services.

There are synergistic opportunities to fight climate change's effects on soil degradation. For example, there are many conservation practices that can be implemented at the field level to reduce erosion, which can simultaneously contribute to sustainability, improved soil quality, increased yields, carbon sequestration, protection of water quality, reduced emissions of trace gases, and many other ecosystem services. We can implement best management practices for water and nutrients and increase economic returns to farmers while contributing to climate change mitigation and adaptation efforts. In addition, temporal updates to conservation tools used in planning

and assessment (e.g., in terms of currently changing rainfall erosivity and management practices) could potentially raise the awareness of producers and land managers, encouraging them to employ adaptive management, targeted conservation, and improved conservation practices more generally.

However, as we adapt to a changing climate, we also need to be aware of the possibility of indirect feedbacks on soil and water resources. For example, the removal of crop residue for biofuel production from annual cropping systems removes valuable residue that is needed to cover the soil and protect it against wind and water erosion. Another example is a shift in crop production toward soybeans across the Midwest, which is a cropping system with a higher potential for soil erosion than corn (O'Neal et al., 2005). As we adapt to climate change, we need to consider potential responses from the system to changes in management. Although climate change can significantly impact soil erosion potential, diminishing productivity, we could implement conservation practices and adapt to a changing climate in a coordinated effort that could minimize this negative impact (Delgado et al., 2011). With proper land use and management, using conservation tools already available to us, we can protect the soil resource under a changing climate within a shifting production and management environment. We need to be aware of the close relationships between climate change, management, and conservation practices in order to implement appropriate tools and policies for addressing the problems being encountered.

The primary agency responsible for implementing conservation policy on nonfederal lands in the United States is the USDA Natural Resources Conservation Service (USDA-NRCS). The NRCS is focusing global climate change efforts in the areas of "(1) quantifying the effects of conservation practices on greenhouse gas emissions and carbon sequestration; (2) refining incentives in conservation programs to address the effects of climate change on agriculture; (3) developing and encouraging the use of conservation practices and systems that reduce GHG emissions; and (4) enhancing opportunities to increase farm profitability on the emerging voluntary emissions trading markets" (http://soils.usda.gov/survey/global_climate_change.html). These activities should be encouraged, enhanced, and expanded. On the research and development side, investments in updating and improving the science, technology, and tools for planning and assessment must be made. These include the ability to reflect temporally changing erosion drivers such as rainfall erosivity; geographic and seasonal changes in cropping, management practices, and plant characteristics; and a

deeper understanding of tolerable soil losses and soil quality thresholds as they impact soil productivity, soil health, carbon balance, and ecosystem services.

2.1. Soil erosion: Drivers

2.1.1 Rainfall

The power or capability of a storm or a series of precipitation events to cause soil erosion is defined as "rainfall erosivity." Wischmeier (1959, 1962) evaluated a large data set of erosion to show that rainfall erosivity was highly correlated to "the product term that measures the interaction effect of storm energy and maximum prolonged intensity." Wischmeier's erosivity index, R, is the sum of values of EI_{30} for any series of individual storm events (storms of <12.5-mm total rainfall are excluded as being insignificant), where E, the estimated total rainfall kinetic energy of the storm, is multiplied by I_{30}, the measured maximum 30-min rainfall intensity. Wischmeier's relationship with data from various erosion stations gave r^2 values ranging from 0.84 to 0.98 (Wischmeier, 1962). Thus, for the data used, rainfall erosivity was the prime determinant of total erosion losses at a given agricultural site. In all cases where this relationship has been evaluated against independent erosion data sets, it has been found to be statistically valid (e.g., Campos et al., 1992; Salehi et al., 1991), though slight variations have been suggested (e.g., Petan et al., 2010; Uson and Ramos, 2001), usually suggesting a shorter time period for the maximum prolonged intensity where such data are available. Important to the topic of climate change, Wischmeier clearly showed that total precipitation amount by itself was poorly correlated to soil erosion. More recent physically based soil erosion models, which are based on experiments looking at fundamental processes of erosion, have also shown the importance of rainfall amount and intensity on soil erosion rates (Nearing et al., 1990, 2005; Wei et al., 2007).

2.1.2 Irrigation

The 2004 NASS "Farm and Ranch Irrigation Survey" reported that 21,288,838 ha of U.S. cropland are irrigated: 50.5% is sprinkler irrigated, 43.4% is surface irrigated (about half in furrows), 5.6% is drip or micro-irrigated, and 0.5% is subirrigated (USDA, 2004). Only limited data have been published on irrigation-induced erosion (Reckendorf, 1995; Sojka et al., 2007), but existing data suggest that both sprinkler irrigation and surface irrigation (particularly in furrows) are susceptible to irrigation-induced erosion. Sediment losses of up to 145 Mg ha^{-1} in 1 h (Israelsen et al., 1946), 40 Mg ha^{-1} in 30 min (Mech, 1949), over 50 Mg ha^{-1} in 24 h (Mech,

1959), and annual losses ranging from 1 to 141 Mg ha^{-1} in southern Idaho (Berg and Carter, 1980) have been reported under furrow irrigation. For sprinkler irrigation (center pivot), sediment yields as high as 33 Mg ha^{-1} have been measured (Koluvek et al., 1993). There are largely unrecognized erosion problems associated with drip, subirrigated, or flood irrigation.

2.1.3 Snow and winter processes

In parts of the northern United States and the 4 million ha of cropland in the northwestern United States, soil erosion is integrally related to snow and the process of snow melting and thawing that can contribute to surface runoff and transport of soil off-site (Van Klaveren and McCool, 2010). Higher erosion rates can occur in these cold environments when the snowmelt-associated erosion occurs on thawed soils over a frozen layer or in situations where rainfall occurs also over a frozen layer (Schillinger, 2001; Zuzel et al., 1982). The thawing of soils also contributes to a higher soil erosion potential because of the high soil moisture at the time of thawing, which increases the runoff potential to a lower soil water suction, and also because of the effects of thawing on soil structure and aggregation that increases soil erosion potential (Van Klaveren and McCool, 2010). This is because soil water suction (negative matric potential) on a wet soil induces the equivalent of an effective external stress on soil, which in turn induces high soil shear and tensile strengths (Nearing et al., 1988, 1991). When the suction is very low, soil strength and erodibility decrease dramatically. Although some process-based and plot-scale research on this topic has taken place, at a regional or national scale, there is no data about the rates of soil erosion for snowmelt or rain-on-thawing-soil. The problem has been recognized, but not quantified.

2.1.4 Wind

In simple terms, wind erosion rate is a function of the cube of wind velocity, soil moisture content, surface roughness, cloddiness, field length, and vegetation characteristics (Chepil and Woodruff, 1954; Chepil et al., 1962; Ravi et al., 2011; Skidmore, 1965; Skidmore et al., 1970). The primary region for wind erosion on U.S. croplands cover an extensive region that stretches across the Great Plains from Texas to the northern United States covering from Montana, North Dakota, and western Minnesota (USDA, 2010b), with additional areas in the northwestern United States (Washington and Idaho) along with scattered areas of the intermountain western United States (south-central Colorado–San Luis Valley). Areas of high wind erosion also

occur on grazing lands on parts of the arid and semiarid regions of the western states.

3. CLIMATE CHANGE AND SOIL EROSION

The major factors that impact soil erosion may be grouped broadly into categories of (a) erosivity of rainfall, irrigation, snowmelt, and wind; (b) plants, cropping, and management; (c) soil erodibility; (d) conservation practices; and (e) topography. Of these, the ones most likely to be directly impacted by climate change include (a) erosivity of rainfall, irrigation, snowmelt, and wind; (b) plants, cropping, and management; and (c) soil erodibility, while strategies for adaptation and mitigation of climate change impacts on the soil resource generally fall into the category of (d) conservation practices.

3.1. Changing rainfall erosion

The most direct impact of climate change on rainfall-driven erosion is related to the erosive power of rainfall (Favis-Mortlock and Guerra, 1999; Favis-Mortlock and Savabi, 1996; Nearing, 2001; Pruski and Nearing, 2002a,b; Williams et al., 1996). Results of process-based soil erosion models indicate that soil erosion responds both to the total amount of rainfall and to differences in rainfall intensity; however, the dominant variable appears to be rainfall intensity and energy rather than rainfall amount alone (Nearing et al., 2005), which is consistent with the empirical natural runoff plots results related to rainfall erosivity discussed above (Wischmeier, 1959, 1962). Assuming that climate change increases the rainfall amount and intensity in similar statistical ways, and that these increases are maintained at a temporal scale, the predicted erosion rate will increase by 1.7% for every 1% increase in total rainfall due to climate change, assuming a temporal stationary relationship between the amount and intensity changes (Pruski and Nearing, 2002a).

Global precipitation patterns and characteristics are changing. Increases in atmospheric and earth surface temperatures will lead to increases in evaporation rates of water at the earth's surface and an increase of about 7% per °C in the capacity of the atmosphere to hold moisture (IPCC, 2007; Trenberth et al., 2007). These factors have led to a more vigorous hydrologic cycle, which have influenced precipitation amounts, intensities, frequencies, and extremes. Karl and Knight (1998) calculated an increase in average annual rainfall of 10% between 1910 and 1996 for the United States

as a whole. The IPCC 4th Assessment reported (IPCC, 2007; Trenberth et al., 2007) historical data showing upward trends ranging from 6% to 8% over the twentieth century for the central and eastern United States. However, projections for many areas of the world that are already water stressed, including the southwestern United States, suggest that these areas will experience a drier future (Seager and Vecchi, 2010; Seager et al., 2007).

Several publications have reported that, over the last few decades, rainfall intensities have also increased in many parts of the world, including in the United States. From 1910 to 1996, the increases in total annual precipitation for the United States were due to increases in the frequency of large events occurring in the upper 10 percentile of measured daily values (Karl and Knight, 1998). In the United States, the increases in extreme precipitation events in the form of heavy (>95th percentile), very heavy (>99th percentile), and extreme (>99.9th percentile) were reported to increase at a rate of 1.7%, 2.5%, and 3.3% per decade, respectively, from 1910 through 1999 (Soil and Water Conservation Society, 2003). These reports show that the number of large events is on the rise and that the increases have been the greatest for the most extreme of events. These reports are in agreement with Groisman et al. (2005) that found trends of increased probability of extreme events for many regions outside the tropics. Additionally, the IPPC 4th Assessment Report (Meehl et al., 2007) predicted that for many parts of the globe, general increases in the intensity of precipitation could be expected.

Recently, a multimodel runoff and erosion study investigated the response of seven leading soil erosion models from the United States and Europe to basic precipitation and vegetation-related parameters using common data from one humid and one semiarid watershed (Nearing et al., 2005). That study suggested that if the trends reported above for precipitation in the United States over the last century continue, significant consequences will occur. Given the sensitivities found in the study, if rainfall amounts during the erosive times of the year were to increase roughly as they did during the last century in the United States, the increase in rainfall would be on the order of at least 10%, with >50% of that increase due to changes in storm intensities. If these numbers are correct, and if no amelioration measures were taken, erosion could increase on average across the country by something on the order of 25–55% over the next century. Correspondent increased values for runoff are 23–31%. These general erosion estimates are greater than would be indicated by the 1.7% for every 1% increase in total rainfall (Pruski and Nearing, 2002a) presented above, in large part

because in fact the relationship between total rainfall and rainfall intensity has not been, nor is expected to be, temporally stationary, as discussed in the earlier paragraph. These are estimates based only on national averages; changes will not be the same across the country. Taking these factors into consideration, the studies have shown that even in the regions where the average precipitation is kept at the same amount, the erosion rates will still increase most likely since there will be an increase in event intensities (Pruski and Nearing, 2002b; Zhang et al., 2012).

A second dominant pathway, after changing precipitation, of the influence by climate change is through changes in plant biomass. The mechanisms by which climate changes affect yields and biomass and by which biomass changes impact runoff and erosion are complex (Favis-Mortlock and Guerra, 1999; Pruski and Nearing, 2002b; Williams et al., 1996).

The anthropogenic increases in atmospheric carbon dioxide concentrations act as a fertilizer that increases aboveground plant production rates (Rosenzweig and Hillel, 1998), and they can have other positive effects such as increased soil surface canopy cover and surface ground cover. Biological material in contact with the ground surface (crop residue) has a much greater impact than canopy cover because it not only protects the soil from raindrop splash but also substantively increases surface water flow roughness that reduces both flow velocities and the ability of water to move sediment. On the other hand, increases in soil and air temperatures will trend toward faster rates of residue decomposition due to an increase in microbial activity, with interdependence on the other important variable of soil moisture. More precipitation could also lead to an increase in biomass production. Temperature changes also affect yields and biomass production levels and rates in complex ways. Increasing temperature that contributes to a warmer initial soil activity at planting can contribute to a quicker germination and growth of corn, increasing biomass production, and similarly a longer and warmer growing period may also extend the growing season and the potential for additional biomass production. However, high-temperature stresses as the temperature becomes too high during the growing season, especially if they accompany higher evapotranspiration rates and drier periods (droughts), could contribute to lower biomass production (Auffhammer, 2011; Lal et al., 2012; Lobell et al., 2011; Rosenzweig and Hillel, 1998) or even to crop failure (Lal et al., 2012). As the above discussion shows, the impacts of climate change are complex and interrelated, but in order to maintain soil productivity, a policy of implementation of conservation practices to adapt to climate change must be in place for

good air, soil, and water quality as well as food security (Fig. 2.1 and Table 2.1).

3.2. Changing irrigation erosion

The complex interactions that will occur between irrigated systems and the increased demands that climate change will put on water resources, together with the changes in total rainfall precipitation and intensity (especially for the southwestern United States, with its projected drier future), will determine future changes in irrigated erosion. Additionally, irrigated erosion will also be a function of the increased food demands that will be generated from population growth, if irrigation systems are expanded to increase food

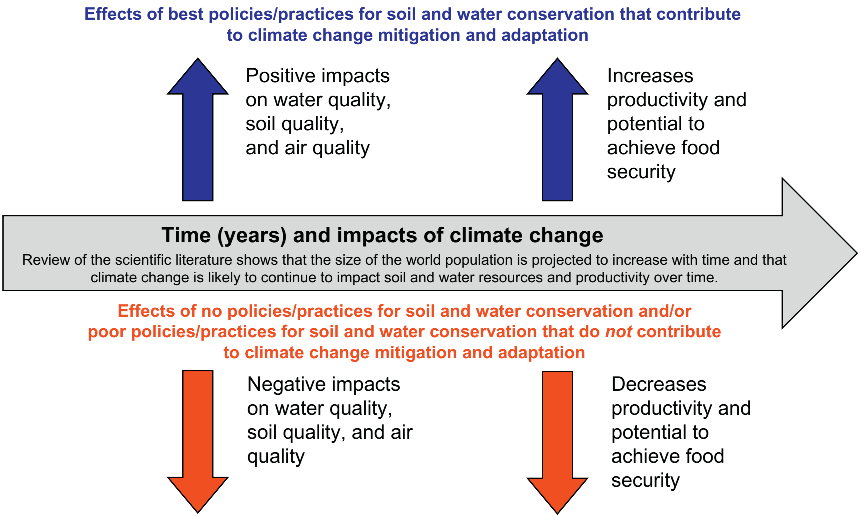

Figure 2.1 There is a close relationship between climate change, limited global water and soil resources, population growth, and food security. As climate change impacts the world's soil and water resources, it threatens to negatively impact food production (i.e., decrease food production and/or food production potential). As the climate changes, conservation practices have the potential to help us achieve maximum sustainable levels of food production, which will be essential to efforts to feed the world's growing population. Good policies/practices for soil and water conservation will contribute to positive impacts on soil and water quality, soil productivity, and efforts toward achieving and/or maintaining food security. These good policies/practices will contribute to climate change mitigation and adaptation. Poor policies/practices for soil and water conservation (or a lack of policies/practices) will contribute to negative impacts on soil and water quality, soil productivity, and efforts toward achieving and/or maintaining food security. *From Delgado et al. (2011).*

Table 2.1 Estimation of the effect[a,b,c] of management practices on soil carbon sequestration (CS), the net flux of nitrous oxide and methane greenhouse gas (GHG) emissions, and the change in upstream and process emissions (UPE, fuel, fertilizer, other)

Management practice[d]	CS	GHG	Additional benefits to the producer and environment	UPE	NCSI
Agroforestry					
Windbreaks for crops and livestock	++	+	Improves crop and livestock protection and wildlife habitat. Provides alternative income source. Has potential to contribute to adaptation (e.g., minimize impacts of extreme wind storms)	+	+++
Silvopasture with rotational grazing	++	+	Provides annual income from grazing; long-term income from wood products. Has potential to contribute to adaptation (e.g., provide a viable income and serve as a tool against a changing climate)	+	++
Riparian forest buffer	++	+	Improves water quality and wildlife habitat. Provides alternative income source (specialty crops, hunting fees). Has potential to contribute to adaptation (e.g., potential to use targeted, strategically located riparian forests to reduce impacts of extreme events due to higher water flow)	+	+++
Livestock					
Organic soil amendments (especially manure)	+	+	Provides nutrients for crops; improves water quality when nutrient management plans are followed and manure is not over applied. Has potential to contribute to adaptation (e.g., potential to result in higher nutrient cycling capacity and soils with improved soil quality that may be able to adapt better and maintain productivity in a changing climate)	+	++
Rotational grazing	++	+	Reduces water requirements. Helps withstand drought. Increases long-term grassland productivity. Has potential to contribute to adaptation (e.g., potential to provide economic alternative due to higher-quality forage)	+	++

Continued

Table 2.1 Estimation of the effect[a,b,c] of management practices on soil carbon sequestration (CS), the net flux of nitrous oxide and methane greenhouse gas (GHG) emissions, and the change in upstream and process emissions (UPE, fuel, fertilizer, other)—cont'd

Management practice	CS	GHG	Additional benefits to the producer and environment	UPE	NCSI
Improve grazing management rangeland	++	+	Potentially increases carbon sequestration on land, depending on previous crop(s) grown. Has potential to contribute to adaptation (e.g., potential to provide economic alternative due to improved grasslands and soils with improved soil quality that may be able to adapt better and maintain productivity in a changing climate)	NA	+
Cropland					
Change from conventional to conservation tillage	+	+	Improves soil, water, and air quality. Reduces soil erosion and fuel use; saves expenses, time, and labor. Has potential to contribute to adaptation (e.g., potential to provide economic alternative due to savings in energy)	+	+
Change from conventional to no-till	+	−	Improves soil, water, and air quality. Reduces soil erosion and fuel use; saves expenses, time, and labor. Has potential to contribute to adaptation (e.g., potential to provide economic alternative due to savings in energy)	+	+
Improved irrigation management	+	+	Improves air quality, reduces water quantity usage. Has potential to contribute to adaptation, since saving water (reduced usage) will be crucial in the coming decades to deal with a changing climate in drier regions and to respond to droughts	+	+
Crop diversity crop rotation	+	+	Reduces erosion and water requirements. Improves soil and water quality, reduces nitrogen and other fossil-fuel-intensive inputs. Has potential to contribute to adaptation (e.g., potential to provide economic alternative that may be able to adapt better and maintain productivity in a changing climate that could bring new pests and diseases due to warmer weather)	+	+

Crop conversion to pasture	++	+	Reduces erosion and increases carbon sequestration. Has potential to contribute to adaptation (e.g., potential to provide economic alternative that may be able to adapt better and maintain economic productivity in a changing climate)	+	+++
Effective nitrogen management (use of slow-release fertilizer, nitrification inhibitors, higher use efficiency, lower rates)	NA	+	Reducing losses of reactive nitrogen can contribute to improved water quality; saves expenses, time, and labor. Can reduce losses via ammonia volatilization	+	+
Cover crops	+	+	Reduces erosion and contributes to soil and water quality. In some cases can contribute to increased economic returns from the following crop. Can be used as biocontrol and reduce chemical inputs. Has potential to contribute to adaptation (e.g., potential to provide economic alternative that may be able to improve yields of subsequent crops and help in weed and pest management)	+	+
Crop conversion to natural	++	+	Reduces erosion and contributes to soil and water quality	+	+++
Improved grazing management	++	+	Reduces erosion and increases carbon sequestration	NA	++
Change from annual to perennial crop	++	+	Reduces erosion and contributes to soil and water quality	+	++

Continued

Table 2.1 Estimation of the effect[a,b,c] of management practices on soil carbon sequestration (CS), the net flux of nitrous oxide and methane greenhouse gas (GHG) emissions, and the change in upstream and process emissions (UPE, fuel, fertilizer, other)—cont'd

Management practice	CS	GHG	Additional benefits to the producer and environment	UPE	NCSI
Biochar application	++	+	Increases carbon sequestration	+	+++
Wetland restoration	++	−	Wildlife and other ecological benefits derived from easement (water quality, flood retention). Has potential to contribute to adaptation (e.g., potential to use targeted, strategically located riparian forest that can be used to reduce impacts of extreme events due to higher water flow)	+	++
Change from annual to switchgrass bioenergy system	+	+	Can serve as a net sink for carbon sequestration across life cycle analysis. Has potential to contribute to adaptation (e.g., potential to provide economic alternative, with improved soil quality that may be able to adapt better and maintain productivity in a changing climate)	+	+
Change from annual to hybrid poplar bioenergy system	+	+	Can serve as a net sink for carbon sequestration across a life cycle analysis. Has potential to contribute to adaptation (e.g., potential to provide economic alternative, with improved soil quality that may be able to adapt better and maintain productivity in a changing climate)	+	+

The majority of this table is adapted from Eagle et al. (2010). Other results from Adler et al. (2007) life cycle analysis of bioenergy systems, and from a matrix of conservation practices developed by USDA-NRCS, West Technology Center were also incorporated, as well as additional comments from the authors of this document. From Delgado et al. (2011).

All estimated values[a,b] were expressed as equivalents of CO_2. A positive, high, and very high sequestration potential are represented by +, ++, and +++, respectively, while net equivalent emissions are represented by −. The net carbon sequestration impact (NCSI) is the sum of CS, GHG, and UPE.

[a] +, ++, and +++ indicates that the mean CO_2 sequestration is 0–2, >2–4, and >4 tons ha^{-1} $year^{-1}$, respectively.

[b] − indicates that there are net emissions of CO_2 at a rate of 0 to 2 tons ha^{-1} $year^{-1}$.

[c] NA indicates that no data were available.

[d] This table presents and compares select conservation practices. We acknowledge that many other conservation practices exist that are not covered in this table, which was presented to show examples of how conservation practices can contribute to climate change mitigation and adaptation.

production as well as the capacity to adopt improved irrigation practices in terms of water use efficiency that could minimize erosion due to increased irrigation demands. For example, water use efficiencies can be increased with improvements in irrigation technology such as use of drip over furrow or sprinkler irrigation. Other factors such as limited irrigation may also impact the irrigated erosion rates for areas where water resources become limited. The use of conservation practices may also increase water use efficiencies. There have been no large-scale studies or reviews to date investigating the anticipated effects of climate change on future irrigation erosion rates. The subject is inherently complex because the main effects will likely be related to direct anthropogenic factors (how producers respond to climate within the context of economic and resource considerations) rather than direct effects of the climate change itself.

3.3. Changing snow-related erosion

Climate change potential impacts can be due to changes in type of precipitation from snow to rainfall. We know that the thawing of soils also contributes to a higher soil erosion potential and higher temperatures with climate change and/or earlier warmer seasons can accelerate the quick melting of snow and snow banks, and increase the runoff potential and potential for higher erosion rates. Higher temperatures not only potentially increase the erosion potential due to the acceleration of the thawing process, but also changes from snowfall to rainfall that are translated into decreased days of snowfall correspondingly increases in days of rainfall, especially if the intensity of these events also increases, can potentially contribute to increase erosion rates by storm runoff. The potential trends in how climate change will impact snow-induced erosion and the effects of snowmelt on thawing soils and of even quicker thawing due to higher temperatures have not been assessed.

3.4. Changing wind erosion

Wind velocities in the Northern Hemisphere, including the United States, have declined slightly in the recent past according to Vautard et al. (2010), who studied data from 822 surface weather stations. They found that annual mean wind speeds decreased on average at a rate of $-0.07 \text{ m s}^{-1} \text{ decade}^{-1}$ on the North American continent, which is an equivalent of about 5% in the past 30 years. Important to the topic of wind erosion, they also found that "strong winds have slowed faster than weak winds." They suggested that the

effect of wind speed changes in general in the Northern Hemisphere may have been due to increased surface roughness due to vegetation increases and secondarily due to atmospheric circulation changes. Though undoubtedly changes in wind speeds would likely be spatially heterogeneous, the study does suggest that major increases in wind velocities in general may not be expected due to climate change. There are no published studies that point to major overall increases in wind speeds in the future.

Major changes in wind erosion rates with climate change would likely be associated with local or regional changes in vegetation and/or soil moisture. Munson et al. (2011) have suggested that wind erosion will increase in grazing lands of the southwestern United States because of increases in aridity associated with the predicted drier future southwestern region that will contribute to a lower soil vegetation cover and higher erosion potential. Field et al. (2010) also suggested that wind erosion could increase in many drylands because of climate change, primarily because of reductions in vegetation cover and also because of intensification of land use. Certainly, also any increases in the incidence of wildfire, which is expected and is in fact occurring now with changes in climate, will increase the rates of both wind and water erosion. Because of the importance of soil moisture to the wind erosion process, wind erosion is most prevalent in subhumid to arid areas. In areas where water is becoming or will become in short supply, abandoned agricultural land in arid, semiarid-irrigated land can be a major source of large wind erosion events. A case in point is the major dust storms that have occurred in southern Arizona on a relatively regular basis in the recent past, including the major event that occurred in the Phoenix area on July 5, 2011.

3.5. Changing agricultural production: Implications for soil erosion

Agricultural production practices will adapt and change in response to climate change. Exactly, how adaptation changes will occur and how fast they will be implemented will depend on a series of complex functions of the changing precipitation amounts and intensities, temperature regimes, atmospheric CO_2 concentrations, economics, and possibly other factors (Delgado et al., 2011; Lal et al., 2011). Nonetheless, some attempts have been made to understand what shifts might possibly occur. For example, Southworth et al. (2000, 2002a,b) used GCM output from the Hadley Center along with various crop models to study potential changes in wheat, corn, and soybean production by 2050 in the Midwest (Indiana, Illinois, Ohio, Michigan, and Wisconsin). Their models projected yield increases of 60–100% for wheat and up to

120% for soybeans in the central to northern part of the region, and little or no increase in the south. Projected increases were in part attributed to direct CO_2 fertilization effects. With existing varieties of maize, they saw decreases in yields across the region, but by switching varieties, they projected the potential for increases in yields in the northern part of the region.

In response to climate change temperatures, the studies also projected significant changes in planting and harvesting dates, as adaptation responses to the climate changes in temperatures, which can certainly have the potential to influence erosion rates especially due to higher precipitation and intensity. The results were coupled to economic modeling (Pfeifer and Habeck, 2002; Pfeifer et al., 2002) in order to assess scenarios of producer adaptation.

O'Neal et al. (2005) took a step further using all the information and conducted a study of climate change impacts on projected runoff and soil erosion in these five Midwestern states (Corn Belt). They assessed several corn–soybean–wheat management scenarios that included planting dates, tillage dates, and harvest dates. Additionally, they also assessed changes in projected land by these three crops across the region, biomass production, and changes in climate such as temperature and precipitation patterns. Their results showed significant increases in runoff and erosion. In 10 of the 11 subregions that were studied the simulated runoff and erosion increased from 10% to 310% and from 33% to 274%, respectively, during the 2040–2059 when compared to the 1990–1999 period. These increased negative environmental impacts were due to several factors, among them a lower corn biomass, lower crop residue, and a shift toward soybean production.

There is a great deal of uncertainty in these projections, but these kinds of increases in erosion rates would be clearly unsustainable in the long term were they to occur. The important point is not the numbers themselves, but that the potential magnitudes of soil erosion change as a function of combined climate change and farmer management adaptation has the potential to greatly exacerbate the climate impacts on soil erosion rates. It is critically important as production systems shift in response to climate change that they are done with the goal of improving conservation management to ameliorate effects of increased precipitation amounts and intensities on soil erosion rather than making them worse.

4. THRESHOLDS OF SOIL EROSION

The soil loss tolerance (*T*) value has been used by the USDA-NRCS in conservation planning since the mid-1960s. This threshold value concept

was first defined by scientists in the 1940s as "the amount of soil that could be lost without a decline in fertility, thereby maintaining crop productivity indefinitely" (Browning et al., 1947; Smith, 1941). Today, the most commonly used definition is "the maximum rate of annual soil erosion that may occur and still permit a high level of crop productivity to be obtained economically and indefinitely" (Wischmeier and Smith, 1978). The *T*-value is used as a basis for comparing estimated soil losses by prediction models to determine whether or not a particular cropping and management system is sustainable. The definition of *T* was tied to soil fertility and maintenance of adequate soil depth for crop production. Implicit in this idea is that rate of soil erosion should not exceed rates of soil formation in the long term.

Soil loss tolerance values range between 2.2 and 11.2 Mg ha^{-1} (1 and 5 tons $acre^{-1}$) for different soil types depending on soil depth and existence of undesirable substrata such as hard rock or a clay pan. Soil loss tolerance values are one of the technical underpinnings to implementation of current U.S. conservation programs because they serve as a target (threshold) to guide the design of farm conservation plans and they are implicit in the definition of "highly erodible lands," which are calculated in part using the *T*-values of the soils. Noncompliance with highly erodible conversion provisions can affect both commodity and conservation program eligibility for producers. Soil loss tolerance values are also used to evaluate the state of the national soil resource in terms of erosion as conducted through the National Resources Inventory (USDA, 2010).

The concepts for soil loss tolerance values were developed for use on cropped soils, and there are questions regarding their applicability to permanent pasture and rangelands (Schertz and Nearing, 2002). Rangelands are often associated with fragile landscapes and a case can be made that their tolerable soil losses should be lower than those on more fertile cropland soils. A better erosion threshold for rangelands, and the current trend in range management in the United States, is probably through the use of Ecological Site Descriptions (USDA, 2003) and associated state-and-transition models (STMs) (Laycock, 1991; May, 1977; Westoby et al., 1989). An ecological site is "a distinctive kind of land with specific characteristics that differs from other kinds of land in its ability to produce a distinctive kind and amount of vegetation" (USDA, 2003). STMs are conceptual models that describe the long-term dynamics of an ecological site, wherein the "states" are identifiable and relatively stable groupings of vegetation species that occupy an ecological site, and the "transitions" cross thresholds from one state to another triggered solely by or in combination with natural events (e.g., drought, fire)

and management actions (either negative—overgrazing, fire suppression or positive—prescribed grazing, brush management) (Westoby et al., 1989). Soil erosion with its associate soil degradation is one of the primary mechanisms by which states may change. Transitions are considered reversible if the preferred state can be achieved using minimal input (e.g., prescribed grazing, brush management) or irreversible if the input needed is energy intensive (e.g., restoring an eroded A-horizon) (Stringham et al., 2003). A typical STM will consist of a reference state that is stable under most natural transitions and alternate states that have varying degrees of degraded ecosystem function and/or increased runoff and erosion.

5. RATES OF SOIL EROSION

The National Resource Inventory (NRI) is a program of assessments that are conducted by the USDA-NRCS (USDA-NRCS, 2010b). NRI summary reports have been published every 5 years since 1982. They provide information on the status and condition of the soil resource for all nonfederally owned lands across the country, including private, tribal, state, and locally owned lands. The inventory is based on ground-collected and remote-sensing data of tens of thousands of sampling points measured each year out of a total of approximately 800,000 total sampling sites established in the 1997 assessment (USDA, 2009). The protocol for erosion estimates in the NRI currently calls for the use of the Universal Soil Loss Equation (USLE) (Wischmeier and Smith, 1978) and the Wind Erosion Equation (Skidmore et al., 1970; Woodruff and Siddoway, 1965) for estimating water and wind erosion, respectively. According to the NRI reports, average erosion rates on U.S. cultivated croplands decreased from approximately 9.9 to 6.7 Mg ha^{-1} (4.4–3.0 tons $acre^{-1}$) and from 8.1 to 5.6 Mg ha^{-1} (3.6–2.5 tons $acre^{-1}$) for water and wind-driven erosion from 1982 to 2007. More than 90% of that reported decrease occurred between 1982 and 1997, primarily because of the increased use of conservation tillage techniques and government-sponsored conservation programs, including the Conservation Reserve Program.

The USLE is used in the NRI rather than the Revised Universal Soil Loss Equation (RUSLE or RUSLE2) in order to allow comparisons of current conditions to those of past years (USDA, 2009). One major difference between the USLE and RUSLE is the use of updated rainfall erosivity maps. The original erosivity map for the USLE applied east of the Mississippi River

was published in 1965 using 22-year station records (Wischmeier and Smith, 1965). The map was extended to the entire continental United States by 1978 (Wischmeier and Smith, 1978). As part of the revision of the USLE (Renard et al., 1997), new data from the time period 1972 through 2002 were analyzed to create new erosivity maps for RUSLE. Though a direct comparison between the two maps is not by any means conclusive, because different data sources were used, there are significant differences between erosivities from the data for the two different time periods, and often the erosivities shown for the later period are significantly greater than from the earlier period.

Angel et al. (2005) used high-resolution temporal data, in part compiled for the revision of the Universal Soil Loss Equation (Renard et al., 1997) to assess changes in annual and seasonal rainfall erosivity over the time period from 1972 through 2002. Results from that study indicated that for the major row crop agricultural regions of the eastern United States, from Florida to Texas to Minnesota to the east coast, there were increasing erosivity trends in fall and winter when fallow farm fields are likely to be vulnerable to erosion. For the interior west, the upper mid-west, and the northeastern United States, upward trends in erosivity were noted for the spring and summer seasons. While some regions in certain seasons did show decreases (most notably at upper elevations along the west coast), the nationwide trends are generally consistent with higher rainfall erosivities.

Although it is understandable that the NRI protocol continues to use the USLE for its assessments of erosion for purposes of comparability, the NRI will not reflect any changes in soil erosion as a function of climate change until updated *R*-factors are used. Additionally, our national assessment of erosion would more accurately reflect climate change impacts over time if it takes into account production changes. The NRI was designed to capture changes in land use and crops grown, which is certainly important, but with the continued use of USLE C-factor tables, the process may not reflect changes in production methods—timing of planting, tillage, and harvest—and biomass production response to atmospheric CO_2 concentrations, which have been shown to be important to determining erosion rates.

5.1. Needed research

Several gaps in knowledge are identified here with respect to our understanding of potential changes in soil erosion rates, as well as soil degradation

rates, as a function of climate change. As it is with water management, so it is with soil conservation planning and assessment: "stationarity is dead" (Milly et al., 2008). Soil erosion prediction tools must be adapted to account for both rainfall erosivity and cropping factor changes as they are used for farm-based conservation planning as well as assessment of the national soil resource base. Furthermore, climate change impact on soil conservation is a complex and integrated problem. We need long-term integrated studies that assess the effects of conservation practices as potential adaptive practices, including the interactive feedbacks of effects on yield, economic returns, climate, water balances, and the effects of precipitation and irrigation on leaching, runoff and erosion, and management implementation factors. While the concept of thresholds has for decades been a part of the discussion of soil conservation goals, under climate change combined with increasing anthropogenic stresses on agricultural production, thresholds are ever more important. We simply do not have the luxury of losing more agricultural ground. While the idea that every ton of soil loss carries with it $2 worth of nitrogen and the farmer cannot afford to lose more than $10 per acre per year in nutrients may have been a rational argument for erosion thresholds in the mid-1950s (USDA, 1956), it is arguably a bit outdated in the twenty-first century. A new contemporary derivation of a soil loss threshold should be derived and might include such factors as (A) the effects of soil erosion rates on the potential to lower soil productivity and the corresponding short- and long-term crop yield economic losses; (B) effects of soil quality, soil health, and ecology that are also closely related to soil productivity and thus maintaining long-term economic returns; (C) climatic feedback implications of soil carbon balance and the effects of soil erosion on off-site losses of soil organic matter as well as the effects of climate change and how conservation practices can contribute to maintain soil organic matter levels needed for long-term sustainability and soil quality; and (D) off-site sediment pollution potential relative to recreation, water supplies, wildlife, associated agrochemicals, costs of dredging, water quality (e.g., the cost to remove nitrate from agricultural sources is estimated to be about 1.7 billion dollars per year; Ribaudo et al., 2011), etc. Similar studies to assess the adaptation alternatives are also needed for natural lands and rangelands where the projected accelerated erosion may disrupt the integrity of soil and ecological processes and decrease the soil quality and productivity for these systems and reduce their ecological diversity. For natural lands and rangelands, the quantification of the relationships between soil erosion and the crossing of such thresholds has been elusive. There is a critical need to

develop techniques to quantify natural erosion rates on stable and degraded ecological sites to define what sustainable erosion rates are for grazing lands.

6. SOIL QUALITY, CARBON, AND PRODUCTIVITY

6.1. Mechanisms

Throughout the scientific peer-reviewed literature, reports can be found of the numerous expected consequences of climate change related to soil quality, soil carbon, and productivity. A long list of authors have reported on these major problems and challenges that threaten future food security, which include increased frequencies and intensities of drought, increases in temperatures that increase evapotranspiration, increases in precipitation intensities, increased hurricane intensities, flooding, increases in soil erosion rates, overexploited aquifers, and other factors (Bryan et al., 2009; Cayan et al., 2010; Delgado et al., 2011; Gleick, 2010; IPCC, 2007; Lal et al., 2011; Madsen and Figdor, 2007; Morton, 2007; Verdin et al., 2005). Since one of the anticipated consequences of climate change and climate variability is an increase in potential soil erosion (Angel et al., 2005; Hatfield and Prueger, 2004; Nearing et al., 2004; SWCS, 2003, 2007), the achievement of food security will necessitate the application of sound management and conservation practices that conserve soil productivity and fertility levels (Delgado et al., 2011; Lal et al., 2011). Delgado et al. (2011) reported that only by choosing to implement conservation programs and/or policies to mitigate and adapt to the impacts of a changing climate will we be able to contribute to the positive changes that will allows us to achieve food security and sustainability, and that without these efforts, food security and sustainability in the twenty-first century will be much more difficult to achieve due to decreases in productivity (Fig. 2.1).

It is well established that erosion decreases soil productivity and that several factors correlated with productivity are negatively impacted by erosion; for example, erosion increases losses of soil organic carbon and other essential nutrients; contributes to reductions in soil fertility levels; lowers soil water-holding capacity; breaks soil aggregates; lowers soil quality; and negatively impacts soil chemical, microbiological, and physical properties (Adams, 1949; Andraski and Lowery, 1992; Bramble-Brodahl et al., 1984; Cruse and Herndl, 2009; Follett and Stewart, 1985; Lal, 1995, 1998; Langdale et al., 1979; Mokma and Sietz, 1992; Quine and Zhang, 2002; Shaffer et al., 1994). Since it is being reported that climate change can increase the potential for soil erosion (Hatfield and Prueger, 2004; Nearing et al., 2004), this is of

great concern because erosion has been reported to lower agricultural productivity across worldwide agroecosystems by 10–20% or even more (Bakker et al., 2004; Cruse and Herndl, 2009; Fenton et al., 2005; Munodawafa, 2011; Quine and Zhang, 2002; Weesies et al., 1994).

Bakker et al. (2004) conducted a detailed analysis of 24 studies that were published during the 1970s to early 2000s examining erosion's effects on productivity and that measured the quantity of lost productivity per amount of eroded soil. From each study, they selected up to a maximum of 12 data points (see Bakker et al., 2004 for additional details about the studies used and how the analysis was conducted). Bakker et al. (2004) divided their analysis by methodology used to assess erosion impacts on productivity such as using (i) comparative plots, (ii) transect methods, or (iii) desurfacing experiments. The Bakker et al. (2004) analysis found that the variability in loss of productivity ranged from a small loss in productivity due to a larger or small loss of soil depth to a large loss in productivity of 95% due to a small loss of soil depth of just 5 cm. They found that the average yield lost across the different methodologies was 4.3%, 10.9%, and 29.6% loss in soil productivity per every 10-cm loss of soil measured with comparative plots, transect methods, and desurfacing experiments, respectively.

We estimated that over 50% of the data presented in graphics by Bakker et al. (2004) were reporting losses in yields greater than 20%, independent of the soil depth that was lost for a given loss in productivity. This clearly shows that erosion is still a worldwide problem that can threaten global food security if left unchecked. Bakker et al. (2004) concluded that the best methodology to represent the effects of erosion was the plot methodology and that an average of 4% loss in productivity per every 10 cm of soil loss should be considered realistic as far as the negative impacts to yield production from erosion. More important was the report from Bakker et al. (2004) showing that the relationship of yield losses to soil depth lost will be convex, so any further losses in soil depth after the first 10 cm of soil lost will become increasingly severe and damaging to soil quality, reducing yield by a greater amount.

The findings from Bakker et al. (2004), together with the projections of higher potential for soil erosion due to climate change, present concerns about the future of the planet and the potential to achieve food security in the twenty-first century for a large and growing population. These findings are in agreement with the Delgado et al. (2011) report that implementation of conservation practices and/or programs to mitigate climate change variability is a must to avoid larger losses in soil productivity. Even with

conservation practices in place, there will be concerns about loss of water resources and changes in the hydrologic cycle that could also affect productivity, but if the soil productivity is reduced due to erosion being left unchecked, the potential to increase yield productivity in the future per unit of land will be reduced and food security will be even more difficult to achieve.

As mentioned above, erosion can negatively impact many factors, such as soil fertility, nutrients, soil organic matter, soil quality, and water-holding capacity, which can contribute to decreased soil productivity (Bakker et al., 2004; Lal, 1995, 1998). We need to acknowledge that there are areas of the field and/or watershed that may be receiving the eroded soil that is transported off-site via the process of soil erosion, and that these areas that may accumulate soil deposits may benefit and have higher yields (Bakker et al., 2004; Lal et al., 2000). However, the general consensus is that even if some areas may benefit from erosion by receiving soil transported from the eroded areas, erosion across the landscape is a process that contributes to overall lower yields across worldwide agroecosystems and contributes to the degradation of soils, and that the potential to achieve food security during the twenty-first century is threatened if we do not minimize soil erosion potential (Lal, 1995, 1998; Montgomery, 2007).

We need to keep in mind that the productivity of agricultural systems will be affected by water balances and/or changes in the hydrologic cycle. For example, it has been projected that increases in the frequency of hurricanes and/or floods in the eastern and northeast United States could affect crop productivity (Madsen and Figdor, 2007), while projected droughts in the southwest could also affect crop and rangeland productivity (Cayan et al., 2010; Gleick, 2010). Independent of the potential to have increased erosion due to high precipitation events or a severe drought that decreases biomass production and increases the potential for wind erosion, projected changes in the hydrologic cycle that ultimately could affect soil profile water balances and plant productivity have been reported (Bryan et al., 2009; IPCC, 2007; Morton, 2007; Verdin et al., 2005). The effects of these hydrological changes could range from a lack of available soil water for plant growth due to droughts to an excess of available water due to flooding (which may not even allow farmers to use their machinery to plant early in the planting season if soils are too wet), to the potential negative effects of nutrient leaching and/or denitrification (Bryan et al., 2009; Cayan et al., 2010; Delgado, 2010; Gleick, 2010; IPCC, 2007; Morton, 2007; Verdin et al., 2005).

There are reports suggesting that with an increase in atmospheric temperatures of 1 °C, there is a potential reduction in yields, not only due to heat stress associated with higher temperatures but also due to the interaction of heat stress and drought stress which reduces the productivity of the cropping systems (Auffhammer, 2011; Lobell et al., 2011; Peng et al., 2004). Evaluations of corn production in Africa suggest that an increase of 1 °C under drought conditions could reduce corn yields by at least 20% (Auffhammer, 2011; Lobell et al., 2011). These studies and analyses show the importance of the development and application of soil and water conservation practices to increase water-holding capacity in the soil profile and/or increase drainage, together with the use of new crop varieties that are more drought resistant, in helping us mitigate and adapt to climate change (Delgado et al., 2011; Lal et al., 2011).

The carbon and nitrogen cycles are associated both with soil productivity and quality and with the potential to mitigate and adapt to climate change. Soil carbon is closely related to many soil functions that are related to productivity, soil quality, and the need to maintain sustainable systems (Doran and Jones, 1996). Increasing carbon sequestration in the soil contributes to the improvement of soil structure and aggregate formation, which increases available water-holding capacity; this increased capacity can potentially be useful in efforts to adapt to climate change, especially during periods of lower precipitation if more water is stored in the soil profile before the drought period. By increasing the soil organic matter, there are also increases in soil porosity which can improve drainage, permeability, and aeration; thus, increasing soil organic matter could be another area where efforts to adapt to climate change variability could be directed.

Carbon sequestration also contributes to increased cation exchange capacity, increased storage of essential crop nutrients (e.g., nitrogen, phosphorous, sulfur, and other macro- and micronutrients), and other properties that will be beneficial in efforts to adapt to the effects of erosion, which can remove nutrients off-site. In summary, soil carbon sequestration is a building block of soil productivity that contributes to higher water-holding capacity, better drainage, higher cation exchange capacity, and better storage of nutrients, which are key factors of soil productivity and long-term sustainability (Doran and Jones, 1996; Lal, 1995, 1999a,b; Lal et al., 1997a,b,c,d; Paul et al., 1997; Stevenson, 1982). As far as nitrogen, the majority of the world's agricultural systems have soils with deficient nitrogen levels and require nitrogen inputs (e.g., nitrogen fertilizers) to maximize crop productivity and economic returns, so practices that help increase carbon and nitrogen

sequestration could also increase the storage and cycling of nitrogen, and are also providing a key nutrient for maximizing productivity.

Agriculture is tied to the carbon and nitrogen cycle; management of agricultural systems with conservation practices makes sense because agriculture not only plays an important role in the flux of greenhouse gases (GHGs) (CO_2, N_2O, and CH_4), totaling 427.5 Tg CO_2 equivalents, or about 6% of the total U.S. GHG emissions (USEPA, 2010), but also helps the systems adapt to conserve their long-term productivity, which is threatened by climate change variability. The most important sources of these trace gases are N_2O emissions from agricultural soil management (215.5 Tg CO_2 equivalents), CH_4 from enteric fermentation (140.8 Tg CO_2 equivalents), manure management, and fossil fuel combusted during farming activities. Sound conservation practices and management could not only serve as mitigation strategies to reduce emissions of N_2O and CH_4 and increase soil carbon sequestration in soils but also provide opportunities to maximize economic returns and long-term productivity. There is a need to transfer and implement these viable mitigation strategies that also contribute to adaptation to climate change.

6.2. Magnitudes of change

When we consider the projected magnitude of change resulting from soil erosion over the next 50 and 100 years, it becomes clear that sustaining civilization will require emphatically choosing to implement soil and water conservation efforts to mitigate and adapt to climate change. Soil and water conservation will be key in maintaining sequestration of soil carbon, as well as in conserving other key macro- and micronutrients needed to maintain the sustainability of agricultural systems in the United States and around the world.

Higher erosion rates in the future could increase the erosion potential to levels higher than the *T*-value threshold, and unless soil and water conservation is implemented to contribute to the maintenance of sustainable soil systems, our soil productivity will be lost at a faster rate and the potential to secure food security will be diminished with time. The carbon in the top surface layer (0–15 cm) is impacted by cultivation, and for agricultural soils in temperate systems, intensive management can contribute to a loss of about 50% over a period of 20–50 years after conversion from natural ecosystems to cultivated sites, and an even faster rate is observed for warmer, tropical systems, which can lose the same amount in just 5–10 years after conversion (Lal, 2004).

Similar reports in the literature show that tillage practices can result in losses of significant amounts of soil organic carbon to different soil depths, such as the 36% total soil organic carbon lost for the top layer (0–20 cm) over 60 years (Cambardella and Elliott, 1992). Izaurralde et al. (2007) reported that there is a need to improve our understanding of the soil carbon nitrogen balance and fractionate how much carbon is lost due to oxidation versus how much carbon is lost due to off-site transport via erosion. Izaurralde et al. (2007) conducted long-term simulations to assess the effects of management practices on a watershed in Ohio and concluded that the watershed that was under a plow system was a net source of carbon to the atmosphere, while the watershed with a no-till system was a net carbon sequestration watershed. Although Izaurralde et al. (2007) simulated the off-site transport of soil carbon, they reported that there is a need to further improve the understanding of the role of the deposition of the eroded soil and of the eroded soil organic carbon transported off-site, as far as being a source or a sink for carbon sequestration when transported off-site.

At a field level, where erosion impacts productivity, it is expected that at the projected higher rates of soil erosion, the losses of soil organic carbon and soil quality will be accelerated if we do not adapt to these potential impacts of climate change to minimize these losses. Policies and conservation programs need to consider that the losses of soil organic matter that could occur not only due to soil carbon oxidation due to cultivation but also due to increased potential for off-site nutrient transport via erosion (resulting from a changing climate) could contribute to reduced soil quality and productivity, especially since soil organic matter is correlated with so many important soil functions. With the implementation of conservation practices, soil quality and soil carbon sequestration can be increased significantly. For example, changing from mouldboard plow management to no-till can significantly restore the amount of soil organic carbon lost in the top 10 cm; Edwards et al. (1992) reported an increase by 56% with such a change. Policies that conserve soil organic matter content and minimize erosion could significantly contribute to climate change adaptation.

Similar positive responses to the implementation of conservation tillage have been found at agricultural sites across the globe. Examples for the United States have been reported by Doran (1980), Doran et al. (1987), Rasmussen and Rohde (1988), Tracy et al. (1990), Havlin et al. (1990), Kern and Johnson (1993), Lafond et al. (1994), and Reicosky et al. (1995); examples for Latin America have been reported by Lal (2000) and Sa et al. (2001); and examples for European soils have been reported

by Smith et al. (1997, 1998) to name just a few. Lal (1998) reported on the potential benefits of conservation tillage for humid temperate regions and semiarid tropical regions, reporting that the carbon sequestration potential for temperate regions, at 0.1–0.5 metric tons ha^{-1} y^{-1}, is twice the rate for semiarid tropical regions. Additionally, he reported that the increases in soil organic carbon due to conservation tillage may last for 20–50 years, depending on soil properties, climate conditions, and management. Since conservation agriculture contributes not only to reduced losses of soil organic carbon but also to reduced erosion and off-site transport of soil organic matter, it will be a key mitigation and adaptation strategy to minimize projected increases in erosion during the twenty-first century.

Not only will conservation tillage provide benefits in the long term that will help reduce the projected increases in erosion rates, but the long-term benefits of increasing soil organic carbon for decades will be beneficial for soil quality. Research is needed to determine how the rate of carbon sequestration will be affected by climate change, higher temperatures that could increase soil respiration and oxidation of soil carbon. How the factors of temperature, productivity, biomass production, and the hydrologic cycle are going to interact with each other at the regional level (e.g., wetter northeast United States, drier southwest United States), and the impact of the magnitude of change at each region is not clearly understood. Independent of the interactions of these factors, the principles of conservation agriculture, keeping the soil surface covered, allowing crop residue to remain in the soil, and minimizing soil disturbance as much as possible, look like promising management practices to contribute to the maintenance or increase of soil organic matter, soil quality, and soil productivity while minimizing soil erosion potential, but additional research is needed. As discussed above, conservation agriculture (e.g., no-till), which advocates the maintenance of a permanent cover on the soil surface and minimal soil disturbance, contributes to the conservation of soil quality and the increase of soil organic carbon at the surface horizon, among many benefits.

Over the last decade, some new data have emerged suggesting that full inversion tillage could, under some circumstances, increase the soil organic carbon at a lower depth such as at the bottom of the plow layer (Baker et al., 2007; Blanco-Canqui and Lal, 2008; Christopher et al., 2009; Six et al., 2002; VandenBygaart et al., 2011; West and Post, 2002). Examples of studies that have reported higher soil organic carbon at the surface horizon with no-till, but found that full inversion tillage showed higher soil organic carbon at the lower depth, include Baker et al. (2007), Blanco-Canqui and Lal

(2008), and Christopher et al. (2009). Several researchers have reported that the problem with the determination of the impact of these practices on deeper soil organic carbon is that there is greater variability at the lower soil depth and that the variability increases with depth (Franzluebbers, 2010; Franzluebbers and Stuedemann, 2007; Gál et al., 2007; Kravchenko and Robertson, 2011; Syswerda et al., 2011). Recent studies by Syswerda et al. (2011) that monitored the effects of no-till and conventional management on surface and deeper horizons (e.g., A/Ap B/Bt and Bts/C horizons) found that carbon sequestration was still slightly higher for the no-till system and significantly higher at the surface A/AP horizon. VandenBygaart et al. (2011) conducted long-term studies for western Canada and found that no-till had higher soil organic carbon at the surface and deeper horizon than the conventional management. However, for eastern Canada, VandenBygaart et al. (2011) found that although no-till had higher soil organic carbon at the surface horizon, the deeper soil horizon had higher soil organic carbon with the conventional tillage, and there was not a net difference between the total soil carbon in the whole soil profile for conventional and no-till.

Although these recent studies compared the surface and deeper soil carbon content and how it was affected by conservation agriculture (in this case, no-till) versus conventional agriculture, there were no measurements presented as far as the off-site transport of soil organic carbon. It is clear that when we consider erosion and the off-site transport of carbon, the plowed (inverse tillage) systems will increase the potential for carbon losses off-site, while conservation agriculture will minimize the off-site transport of soil organic carbon (Izaurralde et al., 2007). If the erosion rates have the potential to increase by 25–55% during this century, as some projections suggest, the potential for off-site transport and losses of soil organic carbon will significantly increase. Additionally, when we evaluate the positive effects of conservation agriculture, we need to consider in the carbon balance that the no-till systems use less energy than conventional systems, which will result in lower CO_2 emissions from operation of machinery that relies on the burning of fossil fuels. When considering off-site transport due to erosion and emissions associated with the burning of fossil fuels, conversation agriculture has been reported to have a net carbon sequestration effect versus inverse tillage agriculture. The more concerning effect is the loss of productivity that may occur with conventional agriculture, due to a higher rate of erosion that is expected to occur as the climate changes. Although we do need additional research on the effects of these management practices on

surface and deeper horizons, as well as assessments of the fate of the carbon transported off-site, conservation agriculture appears to have potential as a key strategy in mitigating and adapting to climate change to maintain the soil productivity. Based on the results of the majority of studies, we suggest that no-till is a viable practice for mitigating climate change and a tool that generates a large set of environmental benefits such as lowering wind and water erosion, improving soil, water, and air quality, and generating potential for net carbon sequestration, especially, when energy use is considered.

6.3. Thresholds

Several researchers have reported on how to achieve sustainable agriculture while conserving the environment by implementing, among other practices, conservation tillage methods such as no-till and/or minimum tillage, which help protect soil quality and productivity (Govaerts et al., 2009; Huggins and Reganold, 2008; Lal, 2001, 2002, 2004; Reicosky, 2008; Reicosky and Saxton, 2007a,b). For agricultural systems where no-till systems are not viable, there are other conservation practices and new technologies that can be applied to reduce or minimize soil erosion, maintain environmental quality, and maintain or increase food security (Al-Sheikh et al., 2005; Delgado, 2010; Delgado et al., 2007; Govaerts et al., 2009; Lal, 2010; Reicosky, 2008; Reicosky and Saxton, 2007a,b; Reicosky et al., 2010). Doran and Jones (1996) reported on the close relationship between soil quality and soil productivity and how they are closely aligned to soil organic carbon. Across the literature, there are many scientific publications showing how soil organic carbon responds to changes in management practices, including management decisions as far as the type of tillage and management of carbon inputs (e.g., residue), which can significantly impact the soil carbon content at a site (Deen and Kataki, 2003; Doran, 1980, 1987; Doran et al., 1987; Havlin et al., 1990; Kern and Johnson, 1993; Lafond et al., 1994; Lal, 1987, 2003; Liebig et al., 2005; Rasmussen and Rohde, 1988; Reicosky, 2001a,b; Reicosky et al., 1995; Tracy et al., 1990). Lal (1995, 1999a, 2003, 2004) and Lal et al. (2011) reported extensively on how important soil carbon sequestration is for achieving food security for our civilization, since it is closely related to soil quality and productivity and linked to climate change issues that impact agriculture. Lal (1989a,b, 1995, 2003) also reported extensively on how we can apply management practices to reduce land degradation and to contribute to the maintenance of soil fertility and productivity.

Management decisions can be implemented for cropping and grazing systems and for off-site areas such as riparian and wetlands zones that can contribute to climate change mitigation and adaptation (Lal et al., 2011). These management decisions are important for the development of sustainable land management across agricultural lands, forests, wetlands, and riparian lands to help mitigate and adapt to climate change (Lal et al., 2011). It is important that we not only conserve and maintain soil productivity but also improve it, since the per capita arable land in the world is shrinking, especially in Asia, with the population growth in India and China (Lal, 1987, 1989a,b, 1998; Oldeman et al., 1991) that will end up putting more pressure on agricultural world markets for increased production.

An important threshold to be aware of is the *T*-values. We need to maintain sustainable systems and to promote the conservation of the most needed land (the lands with maximum productivity and capacity). We will probably need to go beyond *T*-values for maintenance of soil fertility and soil productivity during the twenty-first century (Cox, 2008; Puckett, 2004). We need to develop a more integrated assessment of thresholds that assesses soil productivity, integrating sustainable erosion as well as other soil functions related to soil quality where we can assign thresholds.

Besides using *T*-values, we could start considering the potential application of the Soil Condition Index, the Soil Management Assessment Framework, and other similar approaches that can help us develop thresholds for soil quality (Cox, 2008; Franzluebbers et al., 2011; Puckett, 2004; Zobeck et al., 2007, 2008). Additional research is needed to identify the relationship between potential soil quality index thresholds and how they will be impacted by climate change that could increase erosion, higher soil temperatures that could increase soil respiration and turnover of soil organic matter, and droughts that could reduce the return of crop residue to the soil surface. These quality indexes assess soil cover, crop residue, and potential carbon sequestration, so there is potential to calibrate these indexes to help develop threshold values beyond *T*.

7. SOIL RESOURCES AND CONSERVATION PRACTICES: MITIGATION AND ADAPTATION

7.1. Mechanisms to control and/or reduce inputs

New technologies that emerged during the Green Revolution have helped us increase food production as population growth has generated increased demand. The challenges of the twenty-first century created by continued

population growth and climate change are creating pressure to find ways not only to increase food production but also to conserve soil and water quality and soil productivity, which are needed to increase food production. Recent publications are bringing attention to concerns that climate change will reduce the potential to achieve and/or maintain food security for the growing world population (Bryan et al., 2009; Delgado et al., 2011; Montgomery, 2007; USDA, 2010; Verdin et al., 2005). There are a large number of examples across the scientific literature about the use of conservation practices and their potential applications for climate change mitigation and adaptation (Charles et al., 2010; Delgado, 2010; Delgado et al., 2011; Eagle et al., 2010; Fraser et al., 2009; Funk and Brown, 2010; Hanjra and Qureshi, 2010; Hu et al., 2005; Johnson et al., 2010; Lal, 2002; Lal et al., 2011; Mu and Khan, 2009; Riebeek, 2010; USEPA, 2010; Warner et al., 2010). Although there are many unknowns as far as how climate change will impact productivity, conservation practices and management provide potential for mitigation and adaptation, and without them, the loss of soil productivity will work against efforts to increase yield per unit of land (Delgado et al., 2011; Lal et al., 2011).

The process in which atmospheric carbon is being fixed by crops via photosynthesis occurs constantly as part of the global carbon cycle and is a key factor in the maintenance of the soil productivity of agricultural systems. The pathway by which the fixed atmospheric carbon can potentially be moved to the soil via translocation to the root systems and, with additional crop residue, return to the soil surface provides opportunities to sequester carbon in the soil. The soil dynamics, soil carbon pools, and how conservation practices can be used to increase carbon sequestration have been discussed in hundreds of papers and a large number of books as well (Follett et al., 2001; Kimble et al., 2007, 2002; Lal, 1998; Lal and Follett, 2009; Lal et al., 1997a,b,c,d; Reicosky, 2001a, 2008; Reicosky and Saxton, 2007b).

Soil and landscape management is part of the carbon cycle, and cultivation of cropping systems can contribute to the oxidation and release of soil organic carbon, reducing its content in the soil carbon pool, and can also contribute to off-site transport due to erosion. Conservation practices and management decisions, such as no-till, minimum tillage, maintaining a high-residue surface cover, use of cover crops, implementing a more permanent cover such as grasslands, or introducing a forage crop such as alfalfa into the rotation, can contribute to the mitigation of climate change by accelerating atmospheric carbon sequestration (Table 2.1; Follett et al., 2000; Lal et al., 1997a,b,c,d). Eagle et al. (2010) conducted an in-depth analysis to

quantify the potential of different conservation practices for climate change mitigation and reported that cover crops, diversifying annual cropping systems, inclusion of perennial crops in rotations, changing from annual to perennial crops, organic soil amendments, reducing fertilizer nitrogen use, change in the type of fertilizer used (e.g., switching to controlled-release fertilizers), nitrification inhibitors, improving grazing management, changing cropland to pasture, cropland conversion to natural areas, and wetland restoration are some practices that can contribute to mitigation. Delgado et al. (2011) reported on not only how conservation practices can contribute to mitigation but also how these conservation practices will be key in contributing to climate change adaptation efforts, especially in the face of potentially higher erosion rates and other climate change issues, if we are to achieve food security during the twenty-first century.

Carbon sequestration will be a key worldwide practice in adapting to climate change and improving so many soil function properties important for increasing soil fertility and productivity. Maintenance of soil cover will also be a key conservation practice for adapting to climate change, especially with the threat of higher erosion rates that will come with extreme weather events associated with climate change. We know that good management and the implementation of sound conservation practices, such as return of crop residue to the soil, minimum tillage, and cover crops, provide the key benefit of contributing to the maintenance of soil cover and reduction of soil erosion, which will be especially important under extreme weather events (Table 2.1). These practices provide benefits such as increasing soil water content and increasing soil permeability, providing higher water storage under drought conditions and contributing to faster drainage of water during high precipitation events. In addition to their potential use in mitigating and adapting to climate change and conserving soil quality, these conservation practices also contribute to the conservation of water and air quality.

One of the important trace gas emission pathways from agricultural systems is N_2O emissions from agricultural soils (USEPA, 2010), and practices that increase nitrogen use efficiency, especially if these higher efficiencies are accompanied by a lower nitrogen application rate, are excellent tools to help lower emissions of N_2O (Eagle et al., 2010; Mosier et al., 2002). Since nitrogen is such a mobile and dynamic element, it can be transported off-site by surface runoff with erosion, and can be leached to water bodies and/or lost via ammonia volatilization, or be lost via pathways that can also contribute to indirect emissions of N_2O off-site (IPCC, 2007). Practices that

increase nitrogen use efficiencies and reduce the off-site transport of nitrogen from agricultural soils contribute to reductions in the indirect emissions of N_2O.

Practices, such as split nitrogen applications, soil testing to account for initial available soil nitrogen, nitrification inhibitors, controlled-release fertilizers, use of cover crops, accounting for nitrogen cycling from the previous leguminous crop residue, and accounting for background nitrogen levels in irrigation water, are examples of practices that can contribute to reductions in nitrogen inputs and thus increase nitrogen use efficiency (Bronson and Mosier, 1993; Bundy and Meisinger, 1994; Cassman et al., 2002; Dabney et al., 2010, 2011; Delgado and Mosier, 1996; Ferguson et al., 1991; Oenema et al., 2001; Robertson and Vitousek, 2009; Rosen and Vomuya, 1999; Shoji et al., 2001; Snyder et al., 2009). These viable practices could contribute to lower nitrogen rates and reduce the direct and indirect emissions of N_2O while maintaining productivity.

Nitrogen leaching, denitrification, surface runoff, and ammonia volatilization can be important pathways for nitrogen losses, but adequate implementation of conservation practices with good nutrient management plans can minimize losses via these pathways (Delgado and Follett, 2010; Follett and Hatfield, 2001; Hatfield and Follett, 2008). Some of the important drivers for these nitrogen loss pathways are tied up to with the hydrologic cycle, temperature, and climate change, where regions will be impacted with higher precipitation events, erosion rates that may increase by 25–55% during this century, and higher atmospheric temperatures; these factors could increase the losses of nitrogen to the environment. The rate of ammonia volatilization can increase with warmer temperatures, while the rate of leaching for coarse-textured soils, and denitrification for finer-textured soils, can increase with high precipitation events such as those that are being predicted will occur with climate change and associated extreme events.

A large number of scientists have conducted extensive research on ammonia volatilization and practices to reduce volatilization losses, and the incorporation of nitrogen is a viable approach often recommended to reduce these losses (Freney et al., 1981; Fox et al., 1996; Sharpe and Harper, 1995; Wood et al., 2000). Similarly, conservation practices, such as conservation tillage, residue management, and cover crops, can keep the surface soil covered and can reduce surface transport of nitrogen (Follett and Hatfield, 2001; Iowa Soybean Association, 2008; Legg and Meisinger, 1982). There are several principles that can be applied to manage nitrogen to minimize nitrate leaching (Meisinger and Delgado, 2002; Robertson

and Vitousek, 2009), and several of these principles can also be used to reduce denitrification losses (Mosier et al., 2002). We have a host of conservation practices and sound nitrogen management decisions that can contribute to increased nitrogen use efficiencies while also helping mitigate the effects of climate change on nitrogen losses (Delgado et al., 2011; Eagle et al., 2010; Lal et al., 2011).

There is a large set of conservation practices that can be applied to increase nitrogen use efficiencies; however, this does not negate the need for management decisions that take site-specific considerations into account, since conservation practices that reduce nitrogen losses via one pathway may increase nitrogen losses via another pathway. For example, incorporation of nitrogen inputs can significantly contribute to increased nitrogen use efficiency by reducing the potential for ammonia volatilization losses (Fox et al., 1996; Freney et al., 1981; Meisinger and Randall, 1991; Peoples et al., 1995), but it may also increase the potential for higher nitrate leaching and/or denitrification since the nitrogen that could have been lost to ammonia volatilization now remains available in the soil. A lower nitrogen rate, especially if the lower rate is applied in split applications to better synchronize the lower N applications with the nitrogen uptake demands of the crop, can reduce both the ammonia volatilization losses and nitrate leaching potential. Some researchers have reported that incorporation increases N_2O emissions (Flessa and Bees, 2000; Wulf et al., 2002), but the depth of incorporation (i.e., shallow versus deep) appears to affect the rate of N_2O emissions (Drury et al., 2006; Liu et al., 2006). Additional research is needed on how to reduce N_2O emissions by incorporation or using new types of fertilizers (Snyder and Fixen, 2012; Snyder et al., 2009).

Some researchers have reported higher nitrogen use efficiencies with spring applications, yet higher N_2O emissions from spring-applied fertilizer, when compared to fall applications (Delgado et al., 1996; Hernandez-Ramirez et al., 2009; Rochette et al., 2004). These findings, which compared fall and spring applications, suggested that the warmer temperatures in early spring (end of March and early April) contributed to high fluxes of N_2O. Research from Wagner-Riddle and Thurtell (1998) and Tilsner et al. (2003) also showed that the fall applications of nitrogen had low and/or minimal N_2O emission peaks during winter, until the warmer months of March and April. Different results were reported by the Hao et al. (2001) study, which found higher fluxes from fall application of fertilizer. Hao et al. (2001) reported a daily flux of 15.4 g N_2O N ha^{-1} day^{-1} for 100 kg N ha^{-1} applied and plowed in the fall, higher than a daily flux of

9.5 g N_2O N g ha^{-1} day^{-1} for 100 kg N ha^{-1} surface applied in the spring. Since other researchers have reported a correlation between plowing and increased N_2O emissions (Mosier et al., 1996), one might expect that the spring-applied fertilizer would have exhibited greater N_2O fluctuation if plowed. Results from several studies comparing spring-applied fertilizer to fall application suggest higher nitrogen use efficiency but higher N_2O emissions flux with spring application (Delgado et al., 1996; Hernandez-Ramirez et al., 2009; Rochette et al., 2004).

Although there is a need for additional research to increase nitrogen use efficiencies and nitrogen cycling while reducing N_2O emissions, there is a strong body of evidence showing that we could use conservation practices and nitrogen management to improve nitrogen use efficiencies while reducing N_2O emissions (Eagle et al., 2010). The use of nitrification inhibitors and controlled-release fertilizers may be able to reduce N_2O emissions and potential losses via other pathways independent of time of application and is an example of climate change mitigation and adaptation (Bronson and Mosier, 1993; Delgado and Mosier, 1996; Shoji and Gandeza, 1992; Shoji et al., 2001; Snyder et al., 2007, 2009). Additional research on the use and development of these nitrification inhibitors and/or new types of nitrogen fertilizer, and how they can be applied in different agroecosystems across the United States for climate change mitigation and adaptation, is still needed (Snyder et al., 2007, 2009).

Delgado et al. (2011) proposed several principles for soil and water conservation for climate change mitigation and adaptation. Lal et al. (2011) reported on the role that management decisions can play in adaptation and mitigation to climate change. Although good management can empower farmers, nutrient managers, and ranchers and allow them to play a role in mitigating and adapting to climate change, each country's conservation programs and policies will be key to achieving food security and increasing productivity (Delgado et al., 2011). Delgado et al. (2011) proposed key principles for mitigation and adaptation such as: (i) surface residue protects, (ii) soil function is improved with soil carbon, (iii) cover the surface, (iv) embrace technology, (v) off-field practices are helpful, (vi) improve landscape diversity with agroforestry, (vii) synergism achieved through multiple conservation practices, (viii) build on within-field tried and true practices, (ix) effectiveness enhanced with landscape-targeting precision conservation, (x) promote energy efficiency, (xi) value water more, (xii) greater diversity needed, (xiii) minimize gas losses, and (xiv) tighter nutrient cycles. There are practices that can contribute to the sequestration of carbon,

reduced erosion rates, reduced emissions of trace gases, and improved soil functions to help farmers better adapt to climate change. Development of new varieties and crop rotations that take changes in the hydrologic cycle into account could also contribute to adaptation. Additional research on how these principles can be applied to climate change mitigation and adaptation in order to maintain economically viable agricultural systems under climate change is needed, including the development of new varieties resistant to drought, high temperatures, flood conditions, and other changes associated with climate change that could impact productivity.

7.1.1 Conservation agriculture: Tillage (no-till/minimum tillage)

Humans have been practicing agriculture for thousands of years and have been cultivating soil to plant crops, increase yields, and even manage water by using tilling systems that increase aeration or furrows that deliver water to crops. Over the millennia, crop rotations, terracing and leveling of land, irrigation, and other practices have been used in combination with tillage. New advances that emerged in the twentieth century (e.g., the green revolution) were accompanied by the use of fertilizers and chemical methods to manage weeds and diseases (e.g., glyphosphate), and new technologies and machinery are contributing to expansion of the adoption of no-till/zero-till systems in some regions of the world, where farmers have seen the economic benefits of using conservation agriculture.

It is widely known that intensive cultivation can lower carbon sequestration and soil quality (Karlen et al., 1994a,b; Lal et al., 1997a,b,c,d; Reicosky, 1997), and if intensive cultivation is left unchecked (i.e., without application of conservation principles), it can contribute to higher erosion rates that degrade the land and lower productivity (Bakker et al., 2004; Lal, 1995, 1998). No-till farming, crop residue management, cover crops, integrated nutrient management, surface residue cover, crop rotations, and other practices can help reduce erosion and increase yields (Lal, 1995, 1998, 2004). Even though implementation of no-till or minimum tillage has been shown to produce very positive results, on a global scale the implementation of this principle of conservation agriculture in terms of the percentage of the world area covered is still low at an estimated 7% (117 Mha) (Derpsch, 2011; Kassam et al., 2009). About 97% of the world area that has no-till is covered by eight countries that have large areas that have adopted mechanized no-till systems: (i) United States, 26.5 Mha; (ii) Argentina, 25.8 Mha; (iii) Brazil, 25.5 Mha; (iv) Australia, 17.0 Mha; (v) Canada, 13.5 Mha; (vi) Paraguay, 2.4 Mha; (vii) China, 1.3 Mha; and (viii)

Kazakhstan, 1.3 Mha. These countries will harvest the long-term benefits of conserving the soil quality across this 7% of the world land area, since they are minimizing erosion and improving soil quality, which will prove highly beneficial under climate change, especially since these areas are being farmed and conserved with minimal soil disturbance. There is a need to expand the implementation of conservation agriculture to a larger world area, wherever it is possible, so that soil productivity will be protected across a larger area. This will be particularly important for future generations that will face greater impacts from climate change and will require higher productivity per unit of land as the world population continues to grow.

Long-term analysis conducted over a 40-year period shows that the emissions of CO_2 are much lower from no-till and reduced tillage than from conventional tillage systems (West and Marland, 2002). These areas totaling 7% of the world area are benefiting from the lower fuel requirements of no-till and/or reduced till systems, which are estimated to be 50% of the fuel requirements of conventional systems that included moldboard plowing (Frye, 1984). Research on the factors that can contribute to adoption of principles of conservation agriculture will be needed in order to expand the land area under these systems. Additional research on the economic benefits of conservation agriculture, including the use of new practices such as precision conservation, precision farming, target conservation, and controlled-release fertilizers, is also needed.

With the challenge that agricultural systems will face during the next 50 and 100 years of increasing productivity to feed a large and growing population that is placing greater demands on the earth's resources, there will be a need for policies that conserve agricultural productivity across the world's key agroecoregions (Delgado et al., 2011; Montgomery, 2007). No-till and/or reduced till systems can reduce soil erosion rates to approximate the long-term rates of soil production, suggesting that they can contribute to more sustainable systems (Montgomery, 2007). FAO (2009) defined conservation agriculture with three basic principles: (1) minimum soil tillage disturbance, (2) diverse crop rotations and/or cover crops, and (3) continuous plant residue cover. These are important principles for conservation of soil and water quality and mitigation and adaptation to climate change.

Although no-till farming is not a "silver bullet" for addressing global climate change, and on occasion it can present some new challenges such as the development of new, resistant varieties of weeds (e.g., glyphosphate-resistant *Palmet amaranth*) that pose a threat to conservation tillage (Price et al., 2011), the use of minimum soil tillage wherever possible, together

with other principles of conservation agriculture, will be needed to conserve critical resources to maintain maximum productivity and help ensure that erosion and lower soil quality do not reduce yield potential. Yield potential will need to remain high and sustainable in order to supply food for the growing population. While it may not be possible to apply conservation agriculture everywhere or for every agricultural system, to the extent possible and economically viable, farmers should integrate all aspects of conservation agriculture into their farming practices as part of agriculture's transition to increased sustainability, and countries will need to implement conservation practices for climate change mitigation and adaptation through conservation programs and policies (Delgado et al., 2011; Fig. 2.1). There is always a need for new research in new emerging areas, as example weed management for mechanized no-till systems (e.g., management to control new resistant varieties of weeds with herbicide rotations, high-residue cover crops, etc.; Price et al., 2011).

7.1.2 Conservation agriculture: Crop residue, rotations, and cover crops

Eagle et al. (2010) reported that crop rotations are a key conservation practice in the mitigation of climate change and can contribute to higher soil carbon sequestration. Using cover crops and/or adding a leguminous crop to the rotation can also increase the potential for nitrogen cycling and for higher nitrogen use efficiencies, reducing the need for fertilizer inputs and contributing to lower N_2O emissions and lower nitrate leaching (Delgado et al., 2010). Delgado et al. (2010) conducted studies using the ^{15}N isotope and reported that the nitrogen lost from the added crop residue during the next cropping season was about 10%, much lower than nitrogen losses from the agricultural systems with the more mobile fertilizer, which was reported to be about 30%. Cropping systems are good conservation tools that can be used to increase nitrogen use efficiencies, reduce nitrate leaching, mine nitrates from groundwater, improve soil and water quality, and contribute to atmospheric carbon sequestration (Al-Sheikh et al., 2005; Delgado et al., 2000, 2010; Meisinger and Delgado, 2002). There is a need for more crop residue exchange studies to assess the use efficiency of crop residue nitrogen across more regions of the United States (Delgado et al., 2010).

Agronomists, conservationists, and farm managers can use crop rotations as a conservation practice and consider the use of drought-tolerant varieties to maximize productivity under drought conditions as an adaptation to climate change. A similar approach could also be used to look for crop rotations

and/or varieties that may be more tolerant to heat stress from higher temperatures as well as short-term flooding conditions for those regions that are projected to have higher precipitation rates in the future. Additional research on the development of new varieties and crop rotations as an adaptation to drought, heat stress, and and/or short-term flooding conditions is needed to adapt to the different effects that climate change will bring to different regions of the country. Research on the potential use of crops with shorter growing seasons and lower water use, and/or the potential to adapt planting time to better fit the hydrological cycle is also needed. Research on the economic viabilities of these practices will also be important.

Recent research shows that the perennial bioenergy crops can contribute to soil carbon sequestration and better protect the environment than systems that are based on grain cropping used for energy (Adler et al., 2007; Eagle et al., 2010; Johnson et al., 2007). A life cycle analysis of these systems shows the advantages of perennial bioenergy crops such as switchgrass and hybrid poplar bioenergy systems that increase net carbon sequestration while minimizing demands for food resources. A large number of scientists have reported that to avoid serious environmental consequences that could come from leaving surface soils unprotected, before crop residue is harvested, there is a need to identify if it is environmentally viable to harvest the residue while still maintaining a sustainable and productive soil with tolerable levels of soil erosion and/or environmental impacts (Cruse and Herndl, 2009; Johnson et al., 2010; Karlen et al., 2009; Lal, 2004; Newman et al., 2010). It is important to remember that erosion rates are projected to increase substantially, while higher temperatures may also increase the rate of decomposition of soil organic matter, so conservation agriculture practices that maintain the soil cover, minimize disturbance, and return residue to the soil to at least maintain soil organic carbon levels (or preferably, increase them) will be important in maintaining the sustainability of cropping systems and mitigating and adapting to climate change (Delgado et al., 2010; Lal et al., 2011). It is important to develop biomass energy systems that are viable and maintain the soil productivity of agricultural systems (Adler et al., 2007; Eagle et al., 2010; Johnson et al., 2007, 2010). There is a need to develop new cropping systems/varieties that will be more efficient in the generation of bioenergy for sustainable biomass energy, while minimizing environmental impacts and competing less with food sources such as grain bioenergy systems.

There is concern that harvesting crop residue from farmers' fields for generation of bioenergy will increase the potential for soil erosion and negatively impact soil productivity, since there is a direct correlation between

maintaining the soil cover and lowering the potential for erosion, as well as a direct correlation between returning crop residue to the field and maintaining higher levels of soil carbon content than if all crop residues are removed. A large number of scientists have reported that when weighing the immediate benefits of harvesting crop residue, managers should also consider the many immediate and long-term benefits that crop residue provides to soil fertility, productivity, and the environment before any crop residue is removed from the field (Cruse and Herndl, 2009; Delgado, 2010; Johnson et al., 2010; Karlen et al., 2009; Lal, 2004; Newman et al., 2010).

Recent work from Meki et al. (2011) suggests that there is potential to use site-specific evaluations and precision conservation to identify areas where crop residue could be harvested with minimal impacts on erosion and soil organic matter content. There is potential to use this site-specific approach that considers the soil type at each field for a precision conservation and precision harvesting (Cruse and Herndl, 2009; Delgado and Berry, 2008; Meki et al., 2011). However, we really need to assess potential long-term impacts since crop residue is an important source of macro- and micronutrients and it contributes to the return of these nutrients to the soil systems (Delgado and Follett, 2002). Recent research suggests that allowing crop residue to remain in the field offers many benefits for conservation and/or climate change mitigation and adaptation (Delgado, 2010; Delgado et al., 2011; Lal et al., 2011) and key soil quality factors (Cruse and Herndl, 2009; Johnson et al., 2010; Karlen et al., 2009; Lal, 2004; Newman et al., 2010).

The benefits from conservation crop rotations are not limited to soil carbon, since they are tools to increase system nitrogen use efficiency that contribute to conservation of surface and groundwater resources. Besides the obvious potential reduction in erosion, conservation rotations (e.g., cover crops, leguminous crops, deeper-rooted crops) can increase system nitrogen use efficiency, increase the subsequent crop's yields, and recover nitrate from the lower soil profile that has been leached from the previous, shallower-rooted crops (Delgado, 1998; Delgado et al., 2001, 2007). Additionally, using these deeper-rooted crops with limited irrigation can be a viable method to increase nitrogen use efficiencies and yields, reduce nitrogen losses to the environment, save significant amounts of water per area, and still have viable economic returns (Delgado et al., 2007). Increasing nitrogen use efficiency will contribute to reductions in the losses of reactive nitrogen to the environment, which have been reported to contribute to acidification and/or eutrophication effects in forests, soils, and freshwater aquatic ecosystems, to contribute to eutrophication and hypoxia in coastal and lake

ecosystems, and to contribute to the depletion of atmospheric ozone, among other environmental impacts (Cowling et al., 2002; Dubrovsky et al., 2010; Goolsby et al., 2001; IPCC, 2007; Mitsch and Day, 2006; Rabalais et al., 2002; Turner and Rabalais, 2003).

7.1.3 Precision agriculture and precision conservation

There is potential to use new technologies to implement precise conservation/nutrient management plans to help us apply conservation practices at the right place in the field and the landscape (by considering spatial and temporal variability) to help us mitigate climate change and adapt to its impacts (Delgado et al., 2011). One of the key areas where we need to help farmers adapt to climate change is nutrient management (i.e., increase production sustainably), and recent publications have shown that nutrient efficiencies can be increased by applying the right input, in the right amount, to the right place, at the right time in the right manner (i.e., 4 Rs; Roberts, 2007). New advancements in technologies have shown that we can reduce nitrogen inputs (which can reduce nitrogen losses to the environment) while increasing nitrogen use efficiencies with precision farming/precision conservation (Bausch and Delgado, 2003; Delgado and Bausch, 2005; Khosla et al., 2002; Kitchen et al., 2005; Scharf et al., 2002).

Just recently, Scharf et al. (2011) showed that sensor-based technology management to apply nitrogen fertilizer outperformed farmers in commercial farm demonstration projects, suggesting that there can be a bright future of improved management that can increase nitrogen use efficiencies, yields, and economic returns. A few years earlier, Delgado and Bausch (2005) showed that by using a remote-sensing approach for precision farming/precision conservation, nitrate leaching losses were cut by half relative to traditional practices under commercial farming systems. Thus, these practices that contribute to higher nitrogen use efficiencies will also contribute to reductions in direct and indirect emissions of N_2O (Eagle et al., 2010).

Additionally, precision (target) conservation can increase the effectiveness of conservation by applying the best practice at the best location (e.g., deep furrows, see Williams et al., 2011; grass waterways, see Luck et al., 2010; Pike et al., 2009) to reduce erosion rates (Berry et al., 2003; Tomer, 2010; Walter et al., 2007). Although there is a degree of variability from field to field, there are fields where the spatial variability of erosion can be substantial, and if this variability is not managed properly, over decades of uniform management, the yields could be decreased considerably (Lobb, 2011; Quine and Zhang, 2002). Precision conservation techniques could

contribute to the implementation of management practices that consider this variability (Luck et al., 2010; Mueller et al., 2005; Pike et al., 2009; Quine and Zhang, 2002; Schumacher et al., 2005; Williams et al., 2011) and can be used for comanagement of soil carbon and nitrogen fertilizer (Pennock, 2005), or even reclaim eroded soils that have lost some of their productivity (Lobb, 2011). New technological advances are allowing for faster application of viable precision conservation practices and are increasing the effectiveness of conservation practices from nutrient application to application of grass waterways, buffers, and conservation reserve program (Dosskey et al., 2002; Galzki et al., 2011; Luck et al., 2010; McConnell and Burger, 2011; Pike et al., 2009; Saleh et al., 2011; Scharf et al., 2011; Williams et al., 2011).

Additionally, tillage operation can move soils from the higher to lower landscape positions after a few decades of cultivation (Lobb, 2011). Precision conservation practices can be used to transport the soil back to the eroded areas to reclaim lost soil fertility and productivity (Lobb, 2011). These precision conservation practices may even serve as mitigation/adaptation practices to reclaim losses in productivity that may increase due to tillage and its interaction with erosion rates that are projected to increase due to climate change.

The use of precision (target) conservation practices that consider spatial and temporal variability could help identify areas that are more susceptible to erosion in the case of extreme events caused by climate change and to improve application of conservation across the field and landscape (Bonilla et al., 2007; Dosskey et al., 2002; Lerch et al., 2005; Mueller et al., 2005; Renschler and Lee, 2005; Schumacher et al., 2005). If erosion rates are projected to increase under climate change, then having the capability to use simulation models to quickly assess the temporal and spatial variability of the potential for erosion at a given site could help in the identification of the areas more susceptible to higher flows of surface water, and the potentially best areas to apply grass waterways (Luck et al., 2010; Pike et al., 2009), buffers (Galzki et al., 2011), and furrows to collect water from runoff (Williams et al., 2011).

A similar approach could also be used to identify the areas of the field that are more susceptible to higher nitrate leaching, and where spatial fertigation applications and management zones can be applied to maximize nitrogen use efficiencies and reduce nitrogen losses (Delgado and Bausch, 2005; Delgado and Berry, 2008; Delgado et al., 2005). The use of these precision (target) conservation practices will contribute to increased water quality of aquifers, lakes, rivers, and other water bodies, since they maximize conservation effectiveness and reduce erosion, as well as reduce losses of nitrogen and phosphorous, and

improve the application of buffers, riparian buffers, and wetlands (Delgado and Berry, 2008; Hey et al., 2005; Khosla et al., 2002; Knight, 2005; Qiu et al., 2007; Sadler et al., 2005; Tomer et al., 2007). It is clear from recent advances in precision (target) conservation that we can implement precision conservation agriculture in a wide range of agricultural systems: from low-tech approaches to help low-input, sustainable systems in Africa (Jenrich, 2011), to high-tech minimum tillage systems that use precision digital elevation data to apply precisely aligned furrows along the contour to capture runoff and reduce erosion (Williams et al., 2011). There is the need to continue to increase our knowledge about how we can expand the use and development of advanced technologies (e.g., computer models, sensors, etc.) to integrate large layers of information so we can apply precision conservation practices across the landscape to mitigate and adapt to climate change. There is the need to develop research that helps us assess the ecosystem services provided by these mitigation and adaptation efforts (e.g., increases in production, economic returns, the conservation of soil and water quality, increased carbon sequestration, and reductions in the emissions of trace gases).

7.1.4 Buffers, riparian buffers, and wetlands

There is potential to use buffers, riparian buffers, and wetlands to adapt to climate change by reducing the off-site transportation of soil, soil organic matter, nutrients, and other agrochemicals, and to reduce the potential for hypoxia by harvesting nutrients, including nitrate, via denitrification (Hey, 2002; Hey et al., 2005; Hill, 1996; Mayer et al., 2007). These conservation practices have been reported as areas that have the capacity to serve as sinks for nutrients moving from upland agricultural fields, preventing movement to streams (Hill, 1996; Mayer et al., 2007; Vidon, 2010). Buffers and vegetative filters can also provide additional economic returns if they can be used for biomass and as a forage source under controlled conditions. The net GHG balance from these practices, especially from wetlands and riparian buffer areas where anaerobic areas can contribute to emission of CH_4 and N_2O, needs to be considered (Conrad, 2007; Kim et al., 2009a,b). Although there is a need for additional research on the net balances of these practices, an analysis by Eagle et al. (2010) with limited data found that agroforestry, buffers, and wetlands restoration contribute to increased net carbon sequestration. Additional research on the effects of using buffers, riparian buffers, and wetlands on the net carbon balance and the emissions of trace gases such as N_2O and CH_4, as well as more research on how shifts in climate change may impact these balances and fluxes, is needed.

7.1.5 Agroforestry

Agroforestry (e.g., alley cropping, silvopasture, riparian buffers, and windbreaks) can potentially be used to sequester carbon and is an excellent conservation practice to mitigate climate change (Eagle et al., 2010; Schoeneberger et al., 2012). Agroforestry could provide other benefits for the environment such as reducing wind erosion when windbreaks are used and/or when intercropping is used to provide a safety net to recover and cycle nitrate that might otherwise leach to groundwater (Allen et al., 2004; Nair et al., 2007; Palma et al., 2007; Rowe et al., 1999; van der Werf et al., 2007). A nitrate recovery response has been reported for cropping systems with deeper root systems following crops with shallow roots, where the deep-rooted crops can even mine nitrate from groundwater (Delgado, 1998, Delgado et al., 2000, 2001). Intercropping trees with crops could potentially create water deficits in the areas of the field where the trees are planted if they use more water than the crop surrounding the trees, especially during the drier season of the year, and areas around trees may have lower yields due to competition for water. However, some agroforestry research indicates that there are also some complementary effects between trees and crops in some cases, which will increase overall productivity (Mercado et al., 2009), so the potential use of intercropping needs to be assessed considering the site-specific conditions of the system, and the practice incorporated where the benefits exceed its costs. Agroforestry could potentially serve as a practice for adaptation to climate change and produce an additional source of income for farmers of low-input systems. Additionally, agroforestry could potentially become a larger source of bioenergy, and new research in agroforestry and its potential benefits for carbon sequestration and other ecosystem services is needed.

7.1.6 Water quantity (including irrigation)

Conservation practices that improve water use efficiency and save water could help use less energy and maximize crop yields, thus increasing crop residue return to the soil surface and underground biomass, contributing to carbon sequestration (Delgado et al., 2007; Eagle et al., 2010). Increases in water use efficiency may allow limited water resources to plant larger areas and to increase total food production for a given region. These increases in water use efficiency will be very important for regions of the United States such as the southwestern United States, which projections indicate will have lower precipitation during the twenty-first century due to climate change accompanied by higher temperatures that will increase evapotranspiration potential.

Additionally, the use of limited irrigation can contribute to the maintenance of yields, maximization of yield production per unit of water use, and/or the use of new, viable cropping systems (e.g., rotations of potato-summer cover crops for hay) while saving large amounts of water, making it a possible climate change adaptation strategy (Delgado et al., 2007; Hu et al., 2005). It is important to keep in mind the strong link that exists between the carbon, nitrogen, and water cycles, and with good irrigation management, there is potential to increase nitrogen use efficiency, thus reducing nitrogen losses (Meisinger and Delgado, 2002; Sadler et al., 2005).

It is clear that conservation practices that increase water use efficiencies are important in several respects: first, saving water will conserve resources for times of drought, and when water demands are increased because of higher temperatures (i.e., higher evapotranspiration). Additionally, increased water use efficiency will also free water resources and make them available to meet the future demands that will be generated by population growth. A highly efficient irrigation system such as drip irrigation contributes to water conservation and net carbon sequestration potential (Eagle et al., 2010). An in-depth analysis conducted by Eagle et al. (2010) found that conversion from dryland to irrigated systems results in higher carbon sequestration in soils, since higher yields and thus more crop residue and belowground biomass are produced, which contribute to soil carbon sequestration. However, when Eagle et al. (2010) conducted a whole system balance accounting for the carbon emissions from fuel, fertilizer, and other sources, the irrigated systems were found to be a net source of carbon emissions when compared to dryland. However, if nitrogen management is improved and nitrogen use efficiencies are increased with nitrification inhibitors and slow-release fertilizers, the lower N_2O emissions will help turn the irrigated systems into net carbon sequestration systems, especially if the irrigated systems use conservation tillage such as no-till, contributing to climate change mitigation and to more sustainable systems with lower potential for irrigation erosion (Eagle et al., 2010).

Water use efficiency for nonirrigated systems can also be increased by using cropping systems and/or varieties that generally use water more efficiently or that extract water from greater depths in the soil profile to use soil water more efficiently; such an approach would be an adaptation to crop stress caused by extreme droughts and higher temperatures. Additionally, there are conservation practices such as mulches, no-till, and keeping the surface covered, which can help capture soil water, reduce evaporation, and/or increase the storage of water in the soil profile, which will be key

to maintaining effective agricultural production in dry systems or systems subject to increased rainfall variability. Other conservation practices that help increase soil organic carbon or benefit the soil functions that improve water-holding capacity (e.g., soil aggregate stability) can contribute to adaptation to climate change.

At the other extreme, the use of conservation practices for water management under excess amounts of water that can create flooding conditions and potentially reduce soil productivity is key in the Midwest. There are several conservation practices, such as controlled drainage, that could potentially increase yields and reduce environmental impacts from agriculture by decreasing the transport of nitrate (Madramootoo et al., 2007; Skaggs et al., 2005; Strock et al., 2010). There are several studies that suggest that conservation practices that increase the infiltration under high precipitation events and/or control drainage of areas under severe precipitation and high water tables will help maximize agricultural production and economic returns for farmers (Strock et al., 2010).

It is well known that tile systems and drainage more swiftly channel nitrate into receiving waters (Randall et al., 2010), allowing less time for N transformation to inert N_2. In the event of climate change where there could be greater precipitation and/or more frequent extreme events, it will be imperative to use drainage control practices, denitrification bioreactors, wetlands, and/or other practices that will minimize the movement of nitrogen and other nutrients to water bodies. There is the need to conduct additional research as far as controlled drainage, reactive barriers, drainage management, and agronomic management to increase yields and nutrient use efficiencies while minimizing nitrogen losses to the environment.

The question of how to manage spatial and temporal drainage variability and how to locate these practices at the best locations in the landscape to increase their effectiveness also requires further research. There is a need to improve the knowledge about the fate and transport of surface carbon and nutrients, as well as subsurface flows of nutrients and how these processes continue (carbon sequestration and emissions of the trace gases CH_4, N_2O) in the drainage ditches, buffers, riparian forests, and wetlands. Increasing nitrogen use efficiencies at the field level so that the potential for nitrogen losses to drainage ditches is reduced and increasing carbon sequestration with conservation agriculture are key approaches to mitigating and adapting to climate change and to developing sustainable systems. The potential use of cover crops to increase nutrient cycling and carbon sequestration is also important and should be studied further. There is consensus that these

conservation practices could help in climate change mitigation and adaptation, but research on how to maximize economic returns for farmers while minimizing environmental impacts is needed.

The projections of a drier southwestern United States with higher evapotranspiration rates are worrisome for the irrigated systems of the western United States, where population growth continues to put additional pressure on water resources that are currently being used for agriculture. Since irrigated agriculture produces yields that can be double or even more than double the yields obtained in the drier, nonirrigated systems of the western United States, these projections for a drier future could create additional pressure to maintain viable productivity across large areas of the western United States, especially regions growing cash crops where water is a limiting factor in maximizing productivity to maximize economic returns. Additional research is needed on how to increase water use efficiencies, which could provide viable alternatives for a region with limited water resources. An example of a viable alternative is the potential to grow summer cover crops with limited irrigation and save great quantities of water, and still have a viable crop for hay, followed with a cash crop that can have higher yields and quality (Delgado et al., 2007). Research on conservation practices such as limited irrigation, more efficient systems such as drip irrigation, and the use of new varieties and/or new, viable cropping systems that may use less water is needed.

Carter (1993) reported that furrow erosion can be significant and contribute to lower crop yields. More efficient water management could contribute to reduced erosion, benefit water quality with reductions in surface runoff and leaching, and result in net improvements in carbon sequestration and soil quality. Another alternative that can be used with better irrigation management to reduce erosion and increase infiltration is the use of polyacrylamide (PAM) compounds (Ben-Hur, 1994; Bjorneberg et al., 2003; Flanagan et al., 2003; Lentz and Bjorneberg, 2003; Lentz et al., 1992). These studies have shown that PAM can potentially be used in conjunction with crop residue management, center irrigation pivots, and other water management conservation practices, to contribute to better infiltration and reduced erosion (Bjorneberg et al., 2003; Lentz and Bjorneberg, 2003). Research in improved use of water budgets is necessary to maintain viable economic production under severe dry periods and times of reduced recharge of groundwater resources.

For regions such as the southwestern United States which have projections for lower amounts of precipitation in the future, a key adaptation to

climate change will be better management of irrigation resources (higher water use efficiency). Maintenance of water resources will be necessary for human quality of life and to maintain economically viable agricultural systems. Water management with controlled drainage and other conservation practices will also be key to maintaining economically viable productivity in regions where precipitation is projected to increase. Soil resource management and conservation of soil quality will be important across all systems, drier or wetter, since the soil is the reservoir of water, and soil quality is directly related to soil productivity. Soil and water management will be key across the United States, and conservation practices could help serve as viable options to manage and conserve soil productivity and help farmers mitigate and adapt to climate change.

7.1.7 Opportunities to reduce methane emissions and capture energy

Manure management is an important source of emissions of trace gases in the United States, which have increased from 29.3 Tg CO_2 in 1990 to 45 Tg CO_2 equivalents in 2008 (USEPA, 2010). There is potential to use conservation practices to reduce these emissions and mitigate climate change. There is potential to trap this gas with biogas/methane digesters to reduce the methane emissions from animal systems (http://www.nrcs.usda.gov/Internet/FSE_DOCUMENTS/nrcs143_026500.pdf; USDA-NRCS CODE 366). This captured methane gas can be used as a source of energy, providing a source of income at the farm, mitigating climate change, and creating a renewable source of energy that is not from fossil fuels. There are opportunities to create digesters that could also receive some organic waste such as manure with water added, manure as excreted, and manure with bedding added. There are different digesters; for additional details see USDA-NRCS CODE 366. Additional benefits of digesters could include the reduction of pathogens in animal manure and improvement in air quality due to reduction and management of odors. Biogas digesters also could provide additional environmental benefits by reducing the amount of manure added to fields.

8. CAN THE EFFECTS OF CLIMATE CHANGE BE AMELIORATED USING PRACTICES?

There is potential to use conservation practices and management to adapt to and mitigate climate change (Delgado et al., 2011; Lal et al., 2011). Conservation practices can help improve soil functions by reducing the potential for soil erosion and increasing soil organic matter, improving

soil quality and increasing the potential for nutrient cycling. With climate change, erosion potential is expected to increase by about 25–50% during the twenty-first century, and conservation practices can be used to reduce and/or minimize erosion impacts due to climate change, contributing to sustainability. Conservation agriculture and the application of principles of conservation practices to mitigate and adapt to climate change will help us avoid some of the negative impacts of climate change on productivity and will help agricultural systems avoid crossing the thresholds as far as the potential for greater soil erosion, which could lower soil quality and reduce soil organic matter. Crop residue retention, no-till and/or minimum tillage practices, and the use of cover crops and crop rotations could help maintain or even improve soil quality (e.g., soil organic matter, soil functions), helping minimize impacts from potentially higher soil temperatures that may accelerate soil organic matter mineralization, which reduces the potential for carbon sequestration.

Some of the most difficult challenges that could arise with climate change are related to impacts on the soil hydrologic cycle and challenges with water management. Conservation practices can improve soil water-holding capacity and storage of water in the soil profile, but extensive periods of drought could significantly impact water availability, reducing potential yields. This issue may not necessarily be overcome with higher water storage in the soil profile, so different crop rotations or the use of crop varieties more resistant to drought will be needed if precipitation patterns are significantly shifted and long drought periods are the more limiting factor. On the other hand, conservation practices, such as drainage systems, wetlands and channels, hilling, and even shifting the planting season, could also help with water management in areas or regions where there is increased precipitation and/or extreme precipitation events have increased in frequency.

9. SUMMARY

Several reports have reported that over the last few decades, rainfall intensities have increased in many parts of the world, including in the United States. From 1910 to 1996, the increases in total annual precipitation for the United States were due to increases in the frequency of large events occurring in the upper 10 percentile of measured daily values (Karl and Knight, 1998). In the United States, the increases in extreme precipitation events in the form of heavy (>95th percentile), very heavy (>99th percentile), and extreme (>99.9th percentile) were reported to increase at a rate of 1.7%,

2.5%, and 3.3% per decade from 1910 through 1999 (SWCS, 2003). These reports show that the number of large events is on the increase and that the increases have been the greatest for the most extreme of events. These reports are in agreement with Groisman et al. (2005) that found trends of increased probability of extreme events for many regions outside the tropics. Additionally, the IPPC 4th Assessment Report (Meehl et al., 2007) predicted that for many parts of the globe, general increases in the intensity of precipitation could be expected.

These same hydrological changes will also include the occurrence of occasional droughts, and for some regions such as the southwestern United States, projections suggest that there will be a decrease in precipitation and a drier region, which will have negative effects on plant productivity and increase the potential for wind erosion. One important adaptation practice will be to consider projected spatial changes in the hydrological cycle, such as wetter and drier regions, and periods of drought. This could help in the development and/or implementation of soil and water conservation policies that consider temporal and spatial effects from climate change at the regional level. These policies should also consider conservation practices that contribute to increased water-holding capacity in the soil profile, improved drainage practices, and the development of new crop varieties and cropping systems that are more resistant to drought (Chen et al., 2012; Delgado et al., 2011; Lal et al., 2011, 2012).

Without good productive soils and the ecosystem, services provided by them to society and life in this planet, the survival of life, and our own species will be in jeopardy. The future changes in climate change that will drive erosion processes will significantly impact soil erosion rates, with higher projected erosion rates for the United States. These higher erosion rates will significantly contribute to lower soil productivity, lower soil organic matter content, lower soil quality, and higher rates of nutrient loss that will contribute to lower the inherent soil fertility needed for maintaining viable economical systems and sustainability. Farmer management adaptations and use of conservation practices to adapt to a changing climate (e.g., no-till practices, crop rotations, precision conservation, crop selection and dates of planting, harvest, and tillage) have the potential to greatly reduce soil erosion rates to adapt to this changing climate. Conservation practices will be key and must be used as strategies for adaptation to climate change impacts on the soil resource. Examples of key strategies are the use of conservation tillage; management of crop rotations and crop residue, including use of cover crops where viable, management of livestock grazing intensities, improved management of

irrigation systems, use of technologies and precision conservation; and many other conservation practices that have the potential to reduce much or all of the potential acceleration of soil erosion rates that might occur under a climate change that will bring more total rainfall with higher intensity rainfall events or potential higher wind erosion rates due to a drier climate.

On February 5, 2013, the USDA released a report about climate change and agriculture stating that by the middle of the twenty-first century, climate change will have a negative effect on major crop and livestock regions of the United States, resulting from higher temperatures and the effects of extreme events (Walthall et al., 2012). Spatial variability of climate change is expected, with a wetter northern and eastern United States and drier conditions for the Southwest and Southern Plains regions (Walthall et al., 2012). The drought of 2012 provided a small window to the future, showing us a glimpse of how changing climate may impact future productivity and how adaptation could potentially lessen this impact in certain cases (Lal et al., 2012). For example, precipitation for the 2011–2012 wheat year was 42% lower than normal in Akron, Colorado, where minimum tillage contributed to storage of water in the soil profile and 30% higher grain production than the conventional tillage system, showing the potential of minimum tillage as an adaptive practice in response to climate change (Lal et al., 2012). However, for the corn-growing season, the drought was catastrophic, and even with minimum tillage, the grain production for 2012 was *zero*, showing that under extreme events of such severity, there could be total crop failure and that even a viable adaptation strategy could fail (Lal et al., 2012). Additionally, water management became a problem due to the drought, and irrigation abandonment occurred in some farms in the South Platte region (northeastern Colorado) and the Arkansas River region (southwestern Colorado) because irrigation water ran out (Allan Andales, personal communication). The drought of 2012 demonstrated that the most important nutrient in agriculture is water; when there is too little water (or conversely, when there is too much), the impacts can be absolutely catastrophic.

Another example of the spatial variability in 2012 is the Pacific Northwest, which has experienced increased precipitation that has contributed to higher yields in this region (Washington and Oregon), where no-till and precision conservation are contributing to climate change adaptation and are reducing the potential for erosion resulting from higher precipitation (David Huggings and John Williams, personal communication). Lal et al. (2012) proposed that the drought of 2012 is an indication that climate change is real and happening now and asks "Are our agricultural policies

compatible with reality?" They also note the critical importance of "continuous and open dialogue between researchers on the one hand and land managers and policy makers on the other." If we are to maintain soil productivity and adapt to climate change in the United States and elsewhere, productivity strategies need to be based on conservation practices such as those described in this chapter and reported by Delgado et al. (2011) and Walthall et al. (2012). The data and review of literature strongly suggest that without conservation practices the survival of our species will be in jeopardy. It is clear that policies and programs that implement conservation practices for climate change adaptation in the United States and elsewhere will be critical to help ensure that natural resources will have the best productivity possible, which will be essential for food security now and through the end of the twenty-first century (Fig. 2.1, Delgado et al., 2011; Walthall et al., 2012; This chapter).

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CHAPTER THREE

Characterization of Organic Matter Composition of Soil and Flow Path Surfaces Based on Physicochemical Principles—A Review

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Contents

Advances in Agronomy, Volume 121
ISSN 0065-2113
http://dx.doi.org/10.1016/B978-0-12-407685-3.00003-7

Abstract

Surfaces of macropores in structured soils can made of clay-organic coatings on soil aggregates or linings on worm burrow or root channel walls. The outermost layer of such surfaces is mostly covered by organic matter (OM), which finally controls sorption properties that are relevant for preferential flow and transport. However, the OM properties and local distributions along flow path surfaces are largely unknown, and methods for analyzing intact surfaces are limited. This chapter reviews the principles and applications of Fourier Transform infrared (FTIR) spectroscopy in comparison with complementary nuclear magnetic resonance technique; it describes FTIR techniques for analyzing the composition of bulk soil OM and of OM fractions and of the millimeter-scale spatial distribution at intact surfaces in structured soils for comparing OM composition with cation exchange capacity of OM and soil wettability. Maps of the millimeter-scale heterogeneous spatial distribution of OM composition at aggregate and burrow surfaces could be obtained with diffuse reflectance FTIR (DRIFT) mapping technique. The distribution of OM composition suggests that sorption properties of the OM and wettability of macropore surfaces are also spatially variable at this local scale. DRIFT mapping technique requires relatively smooth and fine-textured intact sample surfaces; further developments need to account for effects of microtopography on the scattering of infrared light. The results indicate yet unknown implications for preferential flow and transport in structured soil, especially for reactive solutes.

1. INTRODUCTION

The global carbon (C) content within organic matter (OM) of mineral soils is estimated to be about 1550 pg in the upper 100 cm layer (e.g., Bavaye et al., 2011; Powlson, 2005), which is about two times the atmospheric C content (e.g., Baveye, 2007). This amount does not consider organic C (C_{org}) stored in permafrost soils (i.e., 450 pg, Zimov et al., 2006) and peats (i.e., 165 pg, Holmen, 1992). Thus, soil organic matter (SOM) is an important C pool in the global C cycle. The main exchange fluxes for SOM, biomass production and SOM decomposition, are represented by the CO_2 exchange between the soil and the atmosphere (e.g., Kuzyakov, 2011). The soil CO_2 sequestration depends on soil functioning as a sink or as a source (e.g., Gregorich et al., 2005). The important contribution of microbial SOM decomposition is strongly depending on moisture and temperature (e.g., Conant et al., 2012; Dungait et al., 2012; von Luetzow and Koegel-Knabner, 2009).

However, fluxes of dissolved organic carbon (DOC) in soil solution toward ground and surface waters (e.g., Mei et al., 2012; Wagai and

Sollins, 2002) and fluxes of CO_2 in the gas phase (e.g., Gregorich et al., 2005; Xu et al., 2008) toward the atmosphere are normally relatively small in relation to the soil C pool (i.e., the SOM content). Smith et al. (2008) found that the rates of soil organic carbon (SOC) stock changes in response to global warming were highly uncertain because of relatively small net changes in soil C-pools as compared to mostly larger biomass and litter C stocks. For improved understanding, Kuzyakov (2011) suggests linking the investigations of pools and fluxes.

Irrespective of global C cycling problems, the SOM content has been used as an indicator for characterizing and understanding soil management- and land use-induced effects on cropping and soil quality (e.g., Hayes and Clapp, 2001; Stevenson, 1994). The term "soil quality" has been defined (e.g., Karlen et al., 1997) as ". . . the capacity of the soil to perform ecological functions. . . ." The role of SOM in maintaining soil quality has been emphasized by many authors (e.g., Powlson, 1996; Reeves, 1997; Smith et al., 2008; Sposito, 2008; Stevenson, 1994).

The quality of SOM itself depends on the chemical composition (e.g., Gärdenäs et al., 2011; Kögel-Knabner, 2000; Leifeld and Kogel-Knabner, 2005). Differently soluble SOM fractions (or otherwise physically and chemically separated OM fractions) have been used for characterizing management-induced changes in the SOM composition with direct effect on soil properties (e.g., Ding et al., 2006; He et al., 2009; Munoz Garcia and Faz Cano, 2012; Sequeira and Alley, 2011; Simon et al., 2009). Instead of using the methodologically defined SOM fractions, a model for continuous SOM quality distributions was proposed (Bruun et al., 2010) that characterized all the different SOM particles and fractions with respect to density, particle size, or other properties.

The properties of coarse-textured soils are assumed to be more affected by changes in SOM than those of loamy soils (Stevenson, 1985). While the soil texture practically remains the same, the SOM can be affected by land use and soil management with respect to both the content and the composition (Jenkinson, 1988). The SOM has been reported to affect several important soil functions (Van Lauwe and Giller, 2006) such as aggregate stability and storage capacity for water and nutrients (Baldock and Nelson, 2000), the cation exchange capacity (CEC) (e.g., Celi et al., 1997), and the wettability (Capriel, 1997; Chenu et al., 2000). However, relations between SOC content and soil properties could only in certain cases be explained simply by the SOC content (e.g., Horne and McIntosh, 2000). Negre et al. (2002) suggested considering the macromolecular behavior

of SOM that depends on chemical composition and three-dimensional spatial structure of the SOM to explain soil wettability, although the detailed relations are largely unknown (e.g., Bachmann and McHale, 2009; Ellerbrock et al., 2005). The chemical composition of the SOM was found to also control its CEC (e.g., Almendros, 1995; Gressel et al., 1995). In analogy to defined OM (Günzler and Böck, 1990), the negatively charged carboxyl groups in SOM are mainly determining the CEC. Here, the term "SOM composition" describes the type and quantity of functional groups (e.g., carboxyl, alkyl, or hydroxyl groups) and their conformation describing the spatial arrangement at the molecular scale (Morrison and Boyd, 1983). The SOM composition therefore characterizes the functional properties of OM in soil (Stevenson, 1985). Soil type, climatic conditions, land use, crop rotation, and soil management modify the SOM composition indirectly through effects on the water and element balances of the ecosystem (e.g., Antil et al., 2005; Kaiser and Ellerbrock, 2005; Kaiser et al., 2007; von Lützow et al., 2006); the input from crop and root residues (Francioso et al., 2000) and the processes of SOM decomposition (Mathers and Xu, 2003). Such effects on SOM composition can preferably be studied using soils of long-term field experiments (LTFE) (e.g., Quideau et al., 2001) since changes in land use and management will take many years of constant management before a new equilibrium is reached (e.g., Schmidt et al., 2000; West and Post, 2002).

For analyzing OM functional groups, several spectroscopic techniques have been applied, such as infrared (IR), Fourier Transform infrared (FTIR) (e.g., Capriel et al., 1995; Demyan et al., 2012; Gerzabek et al., 1997) or nuclear magnetic resonance (NMR) spectroscopy (e.g., Hayes and Clapp, 2001; Kogel-Knabner, 1997). In the field of organic chemistry, such spectroscopic techniques were used to determine the specific molecular structure of pure, exactly defined organic substances (e.g., Hesse et al., 2005). These techniques are based on the interactions between electromagnetic radiation and the molecular subcomponents (e.g., electrons, magnetic spin of certain isotopes, or molecular bonds) within the functional groups. During the wave–particle interaction, the light transfers a part of its energy on the molecular subcomponents (e.g., Hesse et al., 2005). Such energy transfer will only take place if (Staab, 1964) the energy of the light is proportional to the differences in the energy of the molecular component in the exited minus the basic energy levels (i.e., quantization of energy levels). The energy level of such subcomponents depends on the type of functional groups within the molecule and the possible inter- (i.e., between different

molecules) and intra (i.e., within the same molecule) molecular interactions such as hydrogen bonding or complex formation with polyvalent cations (PC) such as Ca^{2+}, Al^{x+}, Mn^{x+}, or Fe^{x+}.

The intensity of the light of a defined wavelength remains unchanged if certain functional groups are absent. In addition, the interaction between a C═O group and a cation can cause, for example, shifts in the absorption bands of the C═O group in both FTIR and NMR spectra. The information from NMR and FTIR is basically the same, however, due to the different wavelengths; NMR analysis of molecular components is based on the reversal of the orientation of the magnetic spin of certain isotopes, while FTIR is based on the excitation of vibration and rotation of molecular bonds. This overview demonstrates that the spectral techniques have specific challenges and limitation that help to identify and to distinguish SOM functional groups. MacCarthy and Rice (1985) as well as Simpson et al. (1997), among others, used spectral techniques to determine molecular structures for humic acid fractions. In contrast to a defined organic substance, the heterogeneous mixture of operationally defined fractions in SOM is characterized by differing transformation status, degradability, and turnover time (von Lützow et al., 2006) ranging from labile (e.g., microbial biomass) to relatively inert components (Baldock and Nelson, 2000; Stevenson, 1994).

Considering its complex nature, Stevenson (1982) suggested a simplified schematic molecular structure model for SOM that was consisting of different functional groups such as alkyl, carboxyl, and hydroxyl groups (Fig. 3.1). The spectra obtained from analyzing such complex organic substances thus integrate over the spectral properties of all components present in the sample reflecting the OM functional group composition of the mixture.

Note that spectroscopic techniques always provide molecular-level information on the composition of the samples. For analyzing, for instance, the behavior of solutes in a soil profile, upscaling and transformation of molecular information to profile or landscapes scales will become necessary. The use of spectral information involves transformation in effective transport properties (i.e., sorption coefficients) and the consideration of spatial characteristics at the profile scale (e.g., Carter, 2000; Müller et al., 2007); the soil spatial variability in SOM composition is additionally important at the field (e.g., Farenhorst, 2006; Sommer, 2006) and larger scales (e.g., Prechtel et al., 2009; Viaud et al., 2010). For such transformation, it becomes necessary to consider sample preparation and sampling technique, the spatial distribution of SOM composition in soil profile as well as at structural

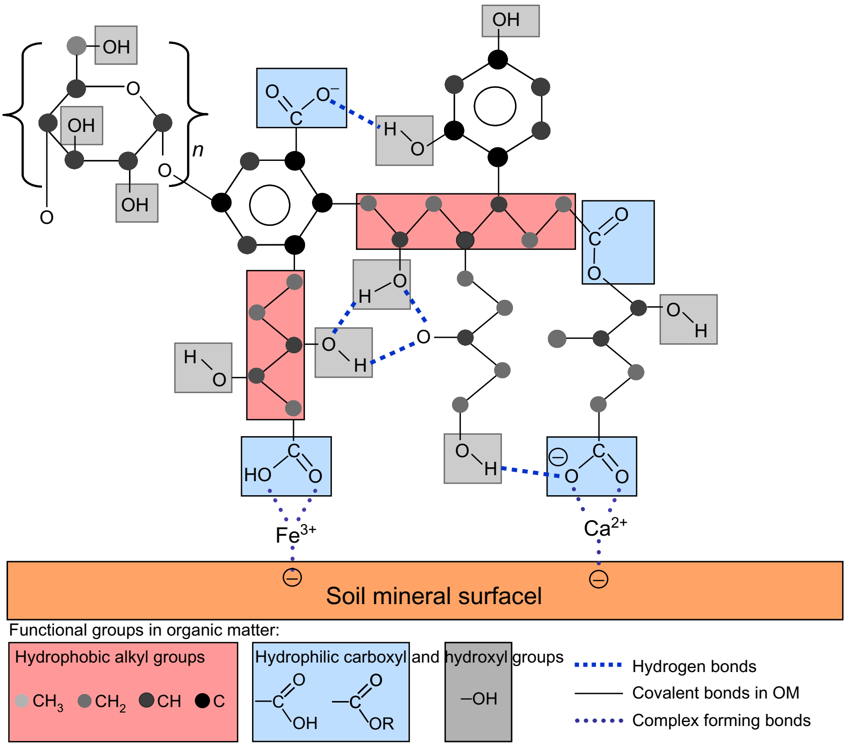


Figure 3.1 A schematic structure for molecules in soil organic matter consisting of alkyl (reddish), carboxyl (bluish), and hydroxyl (no color) groups as well as aromatic rings. The negatively charged mineral surface is complexing the organic molecular structures by polyvalent metal cations such as Ca^{2+}, Al^{x+}, Mn^{x+}, or Fe^{x+}. The bottom scheme is indicating the alkyl groups different in hydrogen saturation; the carboxyl groups that can have OH or OR; R denotes the alkyl chain. *Adapted from Stevenson (1982).*

surfaces together with above-mentioned challenges and limitations of the spectroscopic techniques.

In soils, the CEC and chemical sorption reactivity for dissolved substances generally increase with SOM content (Sposito, 2008; Stevenson, 1994), while the wettability of soil decreases with SOM content in many cases (e.g., Chenu et al., 2000; Jaramillo et al., 2000; Mataix-Solera and Doerr, 2004) with some exceptions explained by differences in the composition of SOM (e.g., Horne and McIntosh, 2000). Such results are for (i) homogeneous soils, (ii) assuming water percolation in a uniform wetting or moisture front with (iii) all available pores and particle surfaces uniformly wetted, and (iv) in contact with the soil solution.

In structured soils, preferential flow may occur along earthworm burrows, root channels, or the interaggregate pore space (e.g., Beven and Germann, 1982; Flury et al., 1994; Ghodrati and Jury, 1992; Nieber, 2000). When moving through such pathways, the percolating water is bypassing much of the volume of the porous soil matrix (for details, see reviews of, e.g., Jarvis, 2007; Köhne et al., 2009a). The rapid movement through small fractions of the soil volume strongly limits the soil's filter and buffer function (e.g., Köhne et al., 2009b). Moreover, any contact and exchange between the preferentially moving water and the surrounding soil matrix is largely restricted to the surface areas of such flow paths. Despite the increasing progress in describing preferential flow processes (e.g., Gärdenäs et al., 2006; Ray et al., 2004; Simunek and van Genuchten, 2008; Simunek et al., 2003), predictions of such processes are limited (Clothier et al., 2008) because it is difficult to determine the soil structural parameters *in situ* (Köhne et al., 2009b). Additionally, the functional properties (e.g., wettability) of surfaces at preferential flow path are hard to analyze; up to now they were quantified for mixed soil samples or for an aggregate packing (Goebel et al., 2008; Ramírez-Flores et al., 2008).

As for mineral particles, the surfaces of porous soil aggregates are mostly covered by OM. Thus, the OM composition at these surfaces may finally control wettability and sorption and transfer properties of flow pathways. The assumption that the spatial variability of water transfer is caused by local differences in wettability of flow path surfaces (Hallett et al., 2004) could be shown by staining experiments (Kodesova et al., 2012; Lipsius and Mooney, 2006). The small-scale local heterogeneity in SOM distribution seems to be of special importance for pesticide transport and chemical sorption processes in structured soils (e.g., Jury and Flühler, 1992; Kaiser and Zech, 1998; White, 1985). While surfaces of aggregates and pores are intensively studied for the mineralogical properties (e.g., Celis et al., 1997; Jongmans et al., 1998; Kaiser and Wilcke, 1996), there are only a few studies on the effect of SOM composition on preferential flow. When analyzing SOM, we need to consider that the spatial distribution of OM in soil is locally highly variable with consequences for turnover rate processes and transport properties (Fig. 3.2A; Leue et al., 2010).

Such small-scale heterogeneity could not be considered when analyzing mixed soil samples (Fig. 3.2B) because the spatial distribution of SOM at preferential flow paths will be lost when mixing the sample. In addition, the spatial geometry of the patchy-like distribution of SOM at structural surfaces is lost. The transport in pathways is local; therefore, the local distribution of both the solution and the solid phase has to be considered for

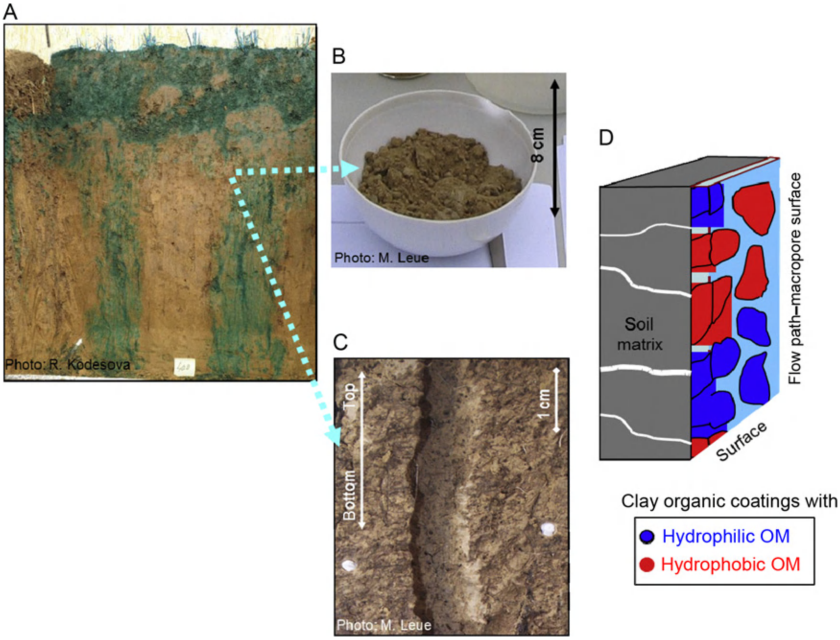


Figure 3.2 Photos of (A) a Luvisol soil profile, (B) a mixed and (C) an intact structural surface sample from a structured soil, and (D) a scheme of the hypothesized spatial distribution of SOM at soil structural surfaces. The Luvisol soil profile is located at the site near Hnevceves, Czech Republic, Brilliant Blue tracer experiment, R. Kodesova, University of Prague.

predictions. Thus, for analyzing the small-scale distribution of SOM at structural surfaces (Fig. 3.2C), it is necessary to investigate intact samples.

Swift (1999) reviewed, for instance, different wet chemical and spectroscopic procedures (FTIR and NMR) for analyzing SOM in bulk soil samples and SOM fractions. However, such investigations were mostly done by different working groups by using either NMR or FTIR except for Inbar et al. (1989) which compared the physical principles of NMR and FTIR for analyzing the same OM fractions from compost samples. The application of the spectroscopic techniques for intact surfaces was yet presented neither in that detail nor in relation to soil physical and chemical properties.

The objective of this review is to discuss the basics of complementary spectroscopic techniques like NMR and FTIR to describe challenges and limitations of spectroscopic techniques and to distinguish between problems caused by soil sample properties, sampling procedure, and basic principles of spectral technique; to describe the application of FTIR techniques for

analyzing composition of (i) defined pure organic compounds, (ii) SOM of mixed soil samples, and (iii) for exploring the small-scale spatial variability of SOM composition at intact structural surfaces (preferential flow path).

The information obtained by FTIR spectroscopy may be related to other soil properties and local two-dimensional (2D) distributions of SOM composition compared with water infiltration to indicate possible use of spectral information for describing SOM properties that are relevant for transformation and transport processes in structured soil.

2. SOM QUANTIFICATION AS SOC

The SOM content makes up about 1–6% of the bulk soil mass of many mineral arable and grassland soils (Stevenson, 1994). Although the fraction is relatively small, SOM is an important component controlling soil physical, chemical, and biological properties. Information on SOM content is usually included in standard soil characterizations together with texture data, among others. The SOM content of soil samples is determined as the content of organic C (C_{org}). However, C_{org} is just one component of SOM besides other elements such as N, S, P, and varying cations in SOM (Sposito, 2008). For converting in general SOM characterizations the measured C_{org} contents to the SOM contents, a relation has been proposed and a factor of about 1.72 (e.g., Nelson and Sommers, 1996) between C_{org} and SOM used. Considering the highly heterogeneous composition of SOM, it is clear that this relation is only an estimate that depends strongly on soil genesis and land use among other factors (e.g., Nelson and Sommers, 1996). Despite these limitations, the widely available C_{org} data have been used for discussing effects of environmental, management, and site factors on amount of SOM as follows: Jenny et al. (1949), for example, compare nitrogen and OM production and decomposition in temperate and tropical soils. The data of this study have been used in more than 400 articles to explain results on increasing organic carbon (OC) contents or litter decomposition among other aspects (Clapp and Hayes, 2006). In a similar way, the data of Jenkinson and Rayner (1977) were used until today. The C_{org} contents were found to depend on climate, soil texture, land use (e.g., West and Post, 2002), crop rotation, and fertilization (Gregorich et al., 2005). The changes in the C_{org} contents of soils could occur on relatively short (Leinweber et al., 1994) and long time intervals (Adani and Tambone, 2005). Most short-term changes in C_{org} contents were possibly restricted to the decomposable OM fractions (e.g., Haynes, 2000, 2005).

Analytically, the C_{org} content is mostly determined (e.g., Nelson and Sommers, 1996; Sposito, 2008) from the difference between total (C_t) and carbonate carbon (C_{CO_3}) as:

$$C_{org} = C_t - C_{CO_3} \tag{3.1}$$

The content of C_t can be determined after dry combustion at 1250 °C (DIN ISO 10694, 1994) by IR detection of CO_2 (e.g., CNS 2000, LECO Ltd.) released from the soil sample. The content of C_{CO_3} has mostly been determined after application of phosphoric acid by gas-chromatographic analysis of carbon dioxide (CO_2) evolution (Nelson and Sommers, 1996); an overview of other methods can be found, for instance, by Chatterjee et al. (2009).

Examples for the change in C_{org} contents have been reported from soils of LTFE located in Bad Lauchstädt, Halle, Müncheberg (Germany) and Rothamstedt (UK). For the 100-year-old fertilization experiment located at Bad Lauchstädt, the C_{org} content of the loamy silt soils was found to be significantly correlated with management practices and crop yields (Körschens and Müller, 1996). Similar relations were observed for the C_{org} contents of the soils in Rothamstedt (e.g., Powlson, 1996). In contrast for the LTFE experiment in Müncheberg located at coarse-textured sandy soils, no significant changes in the C_{org} contents for different fertilizer applications were observed (Ellerbrock et al., 1999a,b). The changes in the C_{org} content of the total soil in response to alterations in land use or management practice are difficult to detect because of variability and heterogeneity.

The C_{org} content changes are mostly small as compared to the generally high background levels and spatial variability in C_{org} contents (Haynes and Beare, 1996; Powlson, 1996). However, when focusing on certain (i.e., preferably labile) C fractions, the changes in these fractional C-contents could be better related to land use or soil management practices and observed in shorter time periods as compared to analyzing the total soil C_{org} contents (e.g., Haynes, 2005). For example, the hot water extracts (e.g., Körschens et al., 1990) were significantly varying between fertilizer applications at the LTFE in Bad Lauchstädt, Thyrow, and Müncheberg and more than for C_{org} total.

3. SOM SEPARATION METHODS

SOM can be separated by physical and chemical procedures (Blazejewski et al., 2005; Hayes, 2006; Stewart et al., 2008) into fractions

different in composition and stability (e.g., Olk and Gregorich, 2006). The SOM fractions can generally be separated into particulate and soluble OM fractions. The term particulate organic matter (POM) has mostly been used to describe a density fraction obtained from particle-size fractions; the term light fraction (LF) defines a density fraction obtained by similar procedures but from the bulk soil (Gregorich et al., 2006).

The SOM fractions have mostly been separated from mixed samples of soil horizons (e.g., von Lützow et al., 2007), while studies focusing more on the process–structure interactions used spatially defined sampling (e.g., Ellerbrock and Gerke, 2004) or even noncontact sensing methods on intact samples (Ellerbrock et al., 2009). The procedures and resulting fractions and the possibilities to characterize SOM composition are summarized in Fig. 3.3. From mixed samples (Fig. 3.3B), the POM, LF, and soluble SOM fractions are characterized as a mean composition integrated over the bulk sample volume. From the spatially defined samples (Fig. 3.3A),

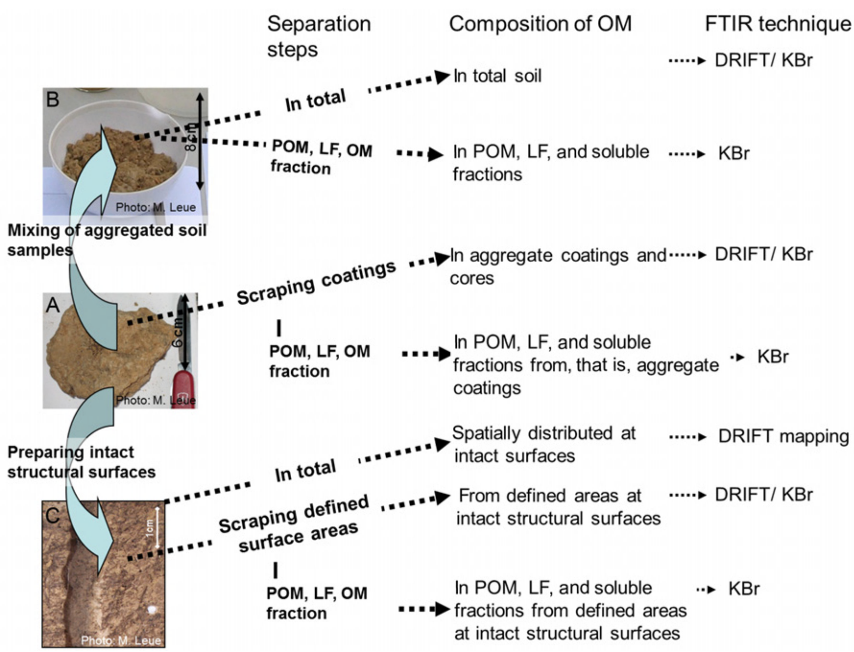


Figure 3.3 Sample preparation steps of aggregated soil: (A) intact structural surface, (B) mixing, and (C) peeling or scraping of coatings in total or from defined surface areas, and procedures for separating POM, LF, and soluble OM fractions from mixed and intact soil samples. The FTIR spectroscopic techniques for analyzing the OM of the different sample types refer to sections 3.1 to 3.4.

the same SOM fractions are characterized only for the sampled regions (e.g., of aggregate coatings). From intact samples (Fig. 3.3C), only the total SOM can be characterized, reflecting a mean composition of all fractions at the sensed surface. The SOM fractions from the various sampling and separation procedures can be used for subsequent spectral analysis (Fig. 3.3), either FTIR or DRIFT to characterize the composition of SOM fractions. One advantage of using SOM fractions for SOM characterization is that the impact of soil mineral components on the spectra is relatively small as compared to using bulk soil (Janik et al., 1995).

In one of the first approaches (Kononova, 1958), soluble SOM fractions were separated from soil by using a 0.1 M sodium hydroxide (NaOH) solution: The resulting solution was then treated with 2 M hydrogen chloride (HCl) to obtain

i. a NaOH-soluble fraction that is insoluble in HCL called *humic acid*,
ii. a NaOH- and HCL-soluble fraction called *fulvic acid*, and
iii. a residue that remains after NaOH treatment called *humins*.

This standard OM extraction with NaOH (e.g., Swift, 1996) has been criticized to strongly alter OM chemical characteristics (e.g., Hayes, 2006) because of the alkaline conditions. At pH values between 12 and 13, for example, saccharides may interact via Maillard reaction with protein components to result in melanoids (e.g., Ziechmann, 1996) and esters can be hydrolyzed, which results in organic acids and alcohols (e.g., Morrison and Boyd, 1983). To reduce possible effects of such alterations, alternative procedures for SOM separation have more recently been developed, which could be grouped into the three basic procedures: (i) density fractionation, (ii) sequential extraction, (iii) sequential oxidation, and (iv) a combination of density and fractionation and sequential extraction.

3.1. Density fractionation

The density fractionation separates POM fractions from soil and soil aggregates. For the physically unprotected POM fractions, heavy liquids of densities between 1 and 2.3 g cm^{-3} have often been used to separate POM from soil and particle-size fractions (e.g., Swift, 1996). Such heavy liquids separate easily decomposable POM from soil samples (Helfrich et al., 2007). The density fractionation procedures are often combined with the supply of dispersing energy (e.g., shaking with glass beads or ultrasonic treatment) (Oorts et al., 2005; Wander, 2004). Ultrasonic treatment, for instance, has been used to distinguish the LF occluded in macro- and microaggregates from the nonoccluded ones (e.g., Swift, 1996).

The POM and LF contents vary in a wide range for the different soils. For arable soils, the LF (i.e., the POM from the particle-size fractions) was found to represent about 1–5% of SOC in mineral topsoil horizons (e.g., Ludwig et al., 2003; Sohi et al., 2001). The content of POM separated from arable soils represented an average of 19% (up to 65%) of SOC, whereas the LF fractions accounted for an average of 6% (up to 36%) while in forest soils, POM was found to represent about 27% in the mean (up to 48%) and LF about 8% (up to 74%) of SOC (Gregorich et al., 2006). The contents of a POM fraction, here separated by electrostatic attraction, were mostly small; values of up to 25% of SOC were found for one forest soil (Kaiser et al., 2009). The POM and LF fractions from mineral topsoil layers were reported to be sensitive to climatic, land use, or management changes because of their relatively fast turnover and close connection to litter input (Bird et al., 2002, 2007). Some authors found that the decomposition rate of POM decreased with size of the sieved fraction where the POM has been separated from Guggenberger et al. (1994a,b). Such relations were used, for instance, in C-turnover models to describe an increase in the mean residence time of differently stable C-pools (Six et al., 1998). The nonoccluded LF was found more easily decomposable by microbes than occluded LF (Roscoe et al., 2004). Charred organic material (i.e., black carbon) in POM (Quénéa et al., 2006) was made responsible for an increase in the mean residence time determined by ^{14}C dating (Baisden et al., 2002; Crow et al., 2007). However, density separation needs to be combined with isotope tracers and detailed chemical characterization as well as other separation techniques for improving models that link SOM dynamics with POM and LF fractions (e.g., Wagai et al., 2009).

Problems associated with fractionation by using heavy liquids such as sodium polytungstate (NaPT) and sodium iodide solutions (Wander, 2004) are caused by (i) triggering solubilization, (ii) altering chemical characteristics, and (iii) promoting C transfers between organic particles and soluble OM fractions (Magid et al., 1996). The separation of organic particles using a NaPT solution of a density of 1.6 g cm^{-3} resulted in organic C losses of 17–26% (Crow et al., 2007). Besides losses through dissolution processes, the dispersions of organo-mineral compounds could affect the separation of organic plant residues or mineral-associated OM (Kaiser and Guggenberger, 2007).

3.2. Sequential extraction procedures

Independent of density and size, SOM can be divided into differently soluble fractions. A number of studies found that their solubility strongly depended

on interactions of SOM with PC and mineral surfaces (e.g., Baldock and Skjemstad, 2000; Kleber et al., 2004; Mikutta et al., 2005b; Sposito, 2008; Stevenson, 1994; Wattel-Koekkoek et al., 2003). Interactions of SOM with PC reduced the solubility of OM in soil (Sposito, 2008). Furthermore, the mineral-associated SOM was frequently assumed to be protected against microbial decay and should therefore be more stable than the water-soluble fractions (e.g., Baldock and Skjemstad, 2000; Gillet and Ponge, 2002; Gregorich et al., 2003; MacCarthy et al., 1990). In contrast, the hot- (Körschens et al., 1990) and cold water- (e.g., Kalbitz et al., 2003) soluble SOM fractions were found more easily decomposable. An acid hydrolysis was proposed for separating more easily decomposable OM fractions such as sugars (Paul et al., 1997). A sodium pyrophosphate (NaPY) solution (Bremner and Lees, 1949) was assumed to yield OM fractions (NaPY-soluble OM) that are stabilized by interactions with PC and clay minerals (Wattel-Koekkoek et al., 2003), oxides and hydroxides (Kaiser and Zech, 1996), and metal–organic complexes (Masiello et al., 2004). During longer extractions ($\geq$24 h), the composition of soil minerals may be affected by the high pH value (i.e., pH of 10) of the NaPY solution (Kaiser and Zech, 1996).

For analyzing differently soluble SOM fractions from the same sample, a sequential extraction procedure was recently proposed by Ellerbrock and Kaiser (2005) combining the water with the NaPY extraction. In a first step, the water-soluble SOM fraction was removed from the sample (water-soluble OM), and in a second step, the sodium pyrophosphate-soluble fraction (NaPYseq-soluble OM) was separated. The OM in the solid residue after the second step was assumed to represent the slowest decomposable fraction obtained by this procedure. The amount and the composition of the sequentially extracted SOM fractions are specific for soil mineral and texture. The water and NaPYseq-soluble fractions amount around 30% up to 50% of SOC (Kaiser and Ellerbrock, 2005; Kaiser et al., 2007). The composition of the sequentially extracted SOM fractions was found useful to distinguish SOM of different soil management and land use (Ellerbrock et al., 1999b, 2001a; Kaiser et al., 2007).

3.3. Sequential oxidation

This approach uses oxidizing substances for a stepwise chemical decomposition of SOM (e.g., Plante et al., 2004). The SOM fractions obtained by the sequential oxidation procedure are assumed to reflect differences in microbial decomposability (Balesdent, 1996); the more rapidly oxidizing fractions are assumed to be more easily decomposable. The CO_2 released during the

oxidation procedure allowed determining OC contents of these SOM fractions (Mikutta et al., 2005a). However, in contrast to SOM fractions obtained by sequential extraction and density fractionation, a spectral characterization of the oxidized SOM fractions is not feasible.

3.4. Combination of density separation and sequential extraction

The combination of the two approaches, density fractionation and sequential extraction, separates the particulate from the soluble OM in a stepwise procedure (e.g., Kaiser et al., 2009). The removal of POM prior to the extraction prevents from an unintended mixing of soluble components in the POM with those of the remaining SOM. To avoid losses of soluble components when separating root residues (i.e., analogy to POM and LF) from soil, Arinushkina (1970, p. 111) applied an electrostatic attraction procedure instead of a density fractionation. Kuzyakov et al. (2001) could separate between 43% for sandy and loamy soils and 35% for a silt loam of the added ^{14}C-labeled roots by using a modified electrostatic method. A preseparation of soil samples in sieved-size fractions improved distinction between organic and mineral particles attracted by electrostatic forces (Kaiser et al., 2009).

The example of the electrostatically separated relatively coarse POM fraction >0.315 mm according to Arinushkina (1970) from an air-dried forest topsoil (Fig. 3.4A) indicates that it consists mainly of fine roots, partly decomposed leaves, and wooden pieces that passed through the 2-mm sieve. The samples from arable topsoils obtained by density fractionation using

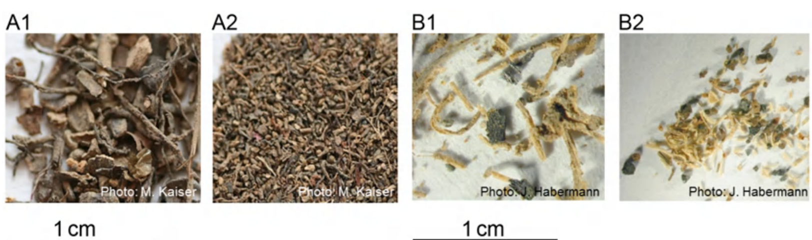


Figure 3.4 Photos of (A) particulate organic matter (POM) separated by electrostatic attraction (Kaiser et al., 2009) and (B) of the light fraction (LF) separated by a density of 1 g cm^{-3} (Kaiser et al., 2007). The particle-size fraction of the POM of the forest soil is 1.25–2 mm (A1) and 0.4–0.5 mm (A2). The LF is from the arable bulk soil of the long-term field experiment in Halle obtained before (B1) and the additionally obtained after (B2) ultrasonic treatments (i.e., showing smaller particles that were occluded in aggregates).

water (Fig. 3.4B) and ultrasonic treatment (Fig. 3.4C) consisted of fine roots as in Fig. 3.4A but no wooden chips. The decomposed leaves in Fig. 3.4C were smaller as those in Fig. 3.4A and B.

4. METHODS FOR DETERMINATION OF OM COMPOSITION

In chemistry, spectral techniques like NMR or FTIR spectroscopy are complementary methods to analyze the composition of *pure and defined* organic components (e.g., Hesse et al., 2005). In general, those techniques act like a question–answer procedure. The question was asked by electromagnetic radiation (light) different in its energy (caused by difference in wavelength). And the answer will be given by the sample: It either interacts with light of certain energy or not, resulting in absorption of light (which causes a decrease in light intensity) or not.

4.1. Physicochemical principles of the methods

The energy of the light (i.e., electromagnetic radiation) is defined by its frequency

$$E = h * v \tag{3.2}$$

with E, the energy of the light (J), h, the Planck's action quantum (J s^{-1}), and v, the frequency of the light (s^{-1}), which is defined by the speed of light, c (cm s^{-1}) divided by the wavelength of the light λ (cm)

$$v = \frac{c}{\lambda}. \tag{3.3}$$

All spectroscopic methods are based on the wave–particle dualism of the light (Hesse et al., 2005). Because of this dualism, light of a certain wavelength could give molecular subcomponents (e.g., atoms, protons, electrons) a push and a probable transfer of energy. During this "push," a molecular subcomponent is shifted toward a higher energy level. Each of these subcomponents has in principle two defined energy levels: a ground level and an excited level. A transfer between ground and excited level takes place if the energy of the electromagnetic radiation is equal to the energy difference between excited and ground level (Hesse et al., 2005). The energy levels of the molecular subcomponents (e.g., magnetic spin of atoms) depend on the physicochemical properties of functional groups, which can be identified.

The transfer of electrons from ground to an excited energy level requires a light with a relatively high amount of energy (e.g., UV or X-ray). The energy content of light required causing vibration and rotation of molecular bonds is much lower (e.g., Raman spectroscopy, FTIR; Hesse et al., 2005). Each spectroscopic technique uses light of different energies affecting different subcomponents within the molecules:

- The IR light causes vibration or rotation of molecular bindings,
- UV–vis (i.e., the UV and the visible light) light causes a transfer of electrons from occupied into nonoccupied orbitals (Hesse et al., 2005), and
- NMR affects the orientation of nuclear spins within an external magnetic field by radio waves (Breitmaier and Voelter, 1989).

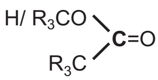
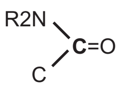
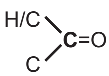
For OM molecules containing C=O groups, for example, the FTIR light is causing a vibration of the double bond between C and O, the UV–vis is causing a "jump" of an electron of the C=O double bond into a nonoccupied orbital, and the radio waves in ^{13}C NMR are causing a change in the orientation of the nuclear spin of a ^{13}C atom in the C=O group. The spectroscopic methods are all based on the same principle; they differ in the wavelength they use and the molecular subcomponents they interact with (Staab, 1964). In all spectroscopic techniques, the intensity of the light absorbed by the sample is determined as a difference in light intensity. For each wavelength, the intensity of the light is registered by a detector yielding a spectrum of the intensities of the light of all wavelength after transfer through the sample.

4.2. NMR spectroscopy

NMR is based on the fact that certain isotopes of H (^{1}H) and C (^{13}C) show a magnetic moment and that the orientation of the corresponding atomic spin within an external magnetic field could be changed by the electromagnetic radiation of a certain wavelength (Hesse et al., 2005). The ^{13}C NMR spectroscopy focuses on the ^{13}C isotope. The magnetic property of a ^{13}C spin depends on the binding status of the corresponding C atom within the organic molecule (Breitmaier and Voelter, 1989). Based on that dependency, ^{13}C NMR spectroscopy allows differentiating the C atoms within a molecule according to their binding status (for determining the type of OM functional groups) because such differences will cause a difference in chemical shift (ppm) of peaks within the ^{13}C NMR spectra related to standards such as tetra-methyl silane (Table 3.1).

The ^{13}C NMR allows analyzing the carbon backbone of organic components for defined organic molecules (Breitmaier and Voelter, 1989). For

Table 3.1 Chemical shift for OM functional groups depending on the position in the molecule and the type of signal in coupled ^{13}C NMR spectra

Functional group	Position in the molecule	Chemical shift (ppm)	Type of signal
Alkyl-C	$H_3\mathbf{C}—C$	0–27	Quartet
	$C—\mathbf{CH_2}—C$	15–45	Triplet
	$C—\mathbf{CH}—C$	20–70	Duplet
O-alkyl	$H_3\mathbf{C}—O$	40–60	Quartet
	$C—\mathbf{CH_2}—O$	40–80	Triplet
	$C—\mathbf{CH}—O$	48–87	Duplet
N-alkyl	$H_3\mathbf{C}—N$	20–55	Quartet
	$C—\mathbf{CH_2}—N$	36–70	Triplet
	$C—\mathbf{CH}—N$	45–75	Duplet
Alkene	$\mathbf{C}{=}C$	90–155	Single
Aromatic	$\mathbf{C}—H$	92–165	Duplet
Carboxylic acid or ester		150–180	Single
Amides		160–185	Single
Aldehydes or ketones		170–205 or 175–225	Duplet or single

Bold phase characters indicate the carbon atoms that cause the chemical shift.
Adapted from Hesse et al. (2005).

illustration, the ^{13}C NMR spectrum of 1-nitro-propylene (Fig. 3.5) has signals at 10–20 ppm that are specific for alky groups, and signals at 130–140 ppm are typical for C=C groups (the signals at 78 ppm are from the solvent: deuterochloroform, and the signal at 0 ppm is from tetra-methyl silane that is used as a reference).

The decoupled ^{13}C NMR example (Fig. 3.5A) indicates that the OM molecule consists of C atoms in three different functional groups: one signal is from an alkyl-C (i) (13 ppm), while two C atoms (ii) and (iii) are within relative similar chemical environments (i.e., two different C atoms in C=C group: one is combined with the nitro group and the second is combined

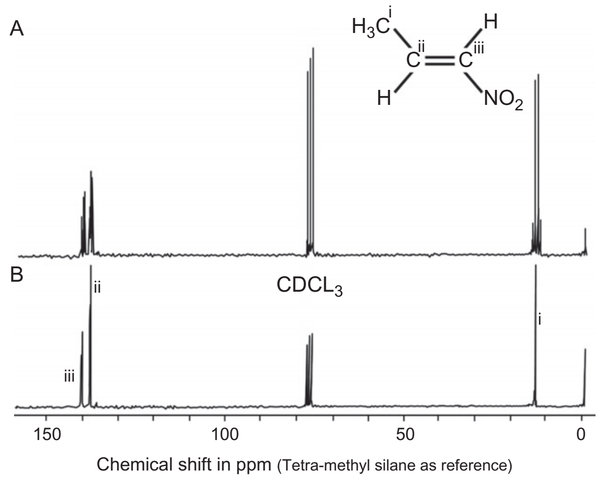


Figure 3.5 (A) Coupled and (B) decoupled ^{13}C NMR spectra (50.3 MHz) of 1-nitro-propylene dissolved in deuterochloroform ($CDCl_3$), measured in 1990 at the Institute of Organic Chemistry, University of Essen with a XL200 NMR spectrometer (Varian). The (i), (ii), and (iii) indicate the marked C atoms in the molecular structure of 1-nitro-propylene, and $CDCL_3$ marks the peaks for C atoms in the deuterochloroform.

with the CH_3 group) that create relative similar chemical shifts (141 and 138 ppm, respectively). For obtaining more information, the spectrum could be used in the coupled mode resulting in a splitting of the signals. Splitting provides information on the combination between C and H atoms (Fig. 3.5B) indicating that the molecule contains one alkyl-CH_3, one CH within the C=C groups that is bond to a NO_2 group, and one to a CH_3 group. Based on such information and the elemental composition ($C_3H_5NO_2$), the structure of the 1-nitro-propylene molecule could be determined as CH_3—CH=CH—NO_2 with ^{13}C NMR.

The signal intensity in NMR spectra is affected by (i) the relaxation time, which is proportional to differences in occupation of different energetic levels, (ii) measurement conditions, and (iii) on the nuclear Overhauser effect (NOE): The NOE causes much higher intensities for H-containing C atoms (Friebolin, 1999) as compared to quaternary C atoms (e.g., COOH), which may result in two times higher intensities especially for CH_3, and CH_2 groups. The ^{13}C NMR signal intensity decreases in the sequence $CH_3 > CH_2 > CH$ in Fig. 3.5. A quantitative interpretation of ^{13}C NMR is possible if the following technical measures are considered (Friebolin, 1999): high pulse power and low signal width, high digital

resolution of the peaks, adequate pulse frequency, and suppression of the NOE (e.g., by addition of paramagnetic elements). However, such measures result in long measurement time of days to weeks for a single sample. Note that the ^{13}C isotopes represent only about 1% of the whole C in a soil sample. The low amount of ^{13}C isotopes in nature limits, especially in case of solid-state ^{13}C NMR analysis, the spectral resolution and complicates the interpretation of the NMR spectra (Breitmaier and Voelter, 1989).

4.3. IR/FTIR spectroscopy

IR and FTIR spectroscopy uses light from 2.5 to 25 μm wavelength. In IR spectroscopy, the light is split into two identical beams running in parallel; one is sent directly through the sample and the measurement chamber and the other is sent only through the chamber to account for the air as the background (Fig. 3.6A). In IR spectroscopy, the light of defined wavelength was sent successively through the sample. In FTIR spectroscopy (e.g., Gottwald and Wachter, 1997), the whole spectrum of IR light is sent directly through the sample in the measurement chamber by using a Michelson interferometer (Fig. 3.6B). The interferometer allows consecutively selecting individual wavelength from the beam. The signals arriving at the detector are collected to obtain an interferogram, which is transformed into an absorption spectrum. The transformation is carried out by using the Fourier transformation and a background correction, accounting for the composition of the air in the measurement chamber. For this correction, a background spectrum has to be measured separately by sending the light beam through the

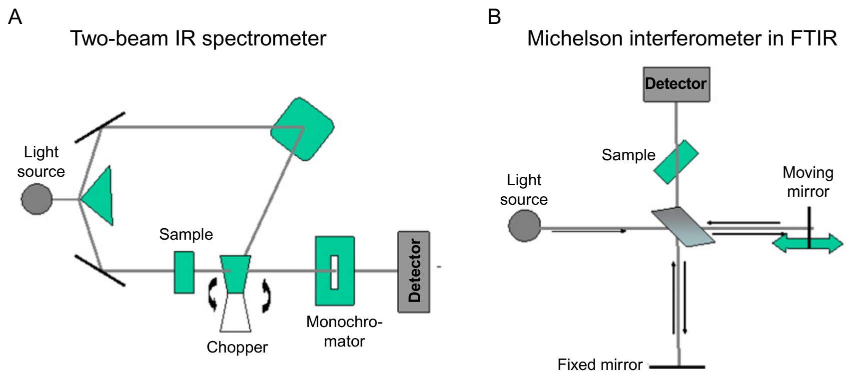


Figure 3.6 Schemes of (A) a two-beam IR spectrometer and (B) a Michelson interferometer within an FTIR spectrometer. *Adapted from Hesse et al. (2005).*

empty measurement chamber. Note that since the 1980s, improved computer technology offers the possibility to use the Fourier transformation as a standard technique so that the FTIR spectroscopy became the common technique (e.g., Hesse et al., 2005).

The spectra of both techniques, IR and FTIR, are similar and the information obtained is identical. While IR spectroscopy yielded analogous spectra usually measured in transmission mode (i.e., light intensity at the detector), FTIR spectra are usually measured in absorption mode (i.e., light absorbed by the sample as the difference between incoming and detected light intensity), and these spectra can also be converted into transmission spectra. The FTIR spectroscopy has the advantage of an independent background correction, a shorter measurement time, and direct analyses such as baseline correction and spectral subtraction (e.g., Senesi et al., 2001).

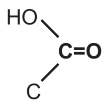
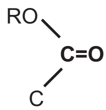
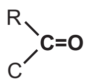
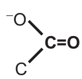
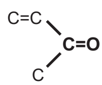
The FTIR spectra show characteristic absorption bands that depend on the type of the molecular bonding in OM functional groups (see Table 3.2 for example). For analyzing solid samples such as soils with FTIR spectroscopy, the following sample preparation techniques could be used (e.g., Hesse et al., 2005):

a. Nujol technique: The sample is mixed with a mineral oil (Nujol) in a thin layer on a flat disk of KBr and covered by a second KBr disk. The sample between the disks is analyzed with FTIR transmission technique (i.e., the IR light is sent through the sample) in absorption mode. Main disadvantage of the Nujol technique with respect to analyzing soil samples is that the overlapping absorption bands of the mineral oil limit the interpretation of the absorption bands of the OM functional groups.

b. Attenuated total reflection (ATR) technique: A small amount of sample on a sample holder is pressed closely against a plane and polished plate of Zn selenide. The IR light is repeatedly reflected at the polished plates while passing the sample (Fig. 3.7A) and finally detected as an ATR spectrum.

This procedure is useful for finely ground or relatively flexible samples like root samples. The spectra (Fig. 3.8, IIA–C) obtained from differently colored regions at a cutting along a fossil reed root (Fig. 3.8, IIA–C) show differences in the absorption bands. The spectrum of the dark colored root edge (Fig. 3.8, IIA) show smaller absorption intensities of CH and CO bands as compared to the spectrum obtained from a region located in the center of the root (Fig. 3.8, IIC). The combination of microscope with ATR technique allows an *in situ* analysis of the surface of such roots samples. The advantage is that ATR requires only small amounts (i.e., <1 mg) of a sample, no addition of chemicals, and short preparation time.

Table 3.2 Absorption bands characterizing OM functional groups in FTIR, the wave number (WN), and the type of vibration and bonding

Classes of substances	Functional groups	WN (cm^{-1})	Type of vibration and type of bonding
Alkyl	**CH_3; CH_2; CH**	2950 to 2850	Asymmetric CH stretching
		2860 to 2800	Symmetric C—H stretching
Polysaccharides	Alkyl-*O*-alkyl (C—O—C)	1150 to1100	C—O stretching
Carboxylic acids		1740 to 1698	C=O stretching
Esters, aldehydes, ketones, amides			R: alkyl chains for esters
			R: H for aldehydes R: alkyl chains for ketones R: amino group for amides
Anionic carboxylic acid groups and carboxylic acid groups conjugated with C=C groups	 	1620 to 1680	C=O stretching
Water, hydroxide, phenols, alcohols		3750 to 2700	OH stretching
Water, hydroxide, phenols, alcohols	O—H; hydrogen bonding	1660 to 1600	OH bonding (i.e., in hydration layers of soil phyllosilicates; Mendelovici et al., 1995; Spaccini et al., 2001)

Bold phase characters indicate the carbon atoms that cause the chemical shift.
Adapted from Hesse et al. (2005).

For highly resolved ATR spectra, however, close contact between the Zn selenide plates and the sample is needed to exclude air. Thus, for inelastic soil samples with particles >0.02 mm, the high pressure needed for the establishing contact may destroy the Zn selenide plates (Kubicki et al., 1999).

c. Potassium bromide (KBr) technique: The finely ground sample is mixed with KBr (i.e., sample dilution <5%) and both again finely

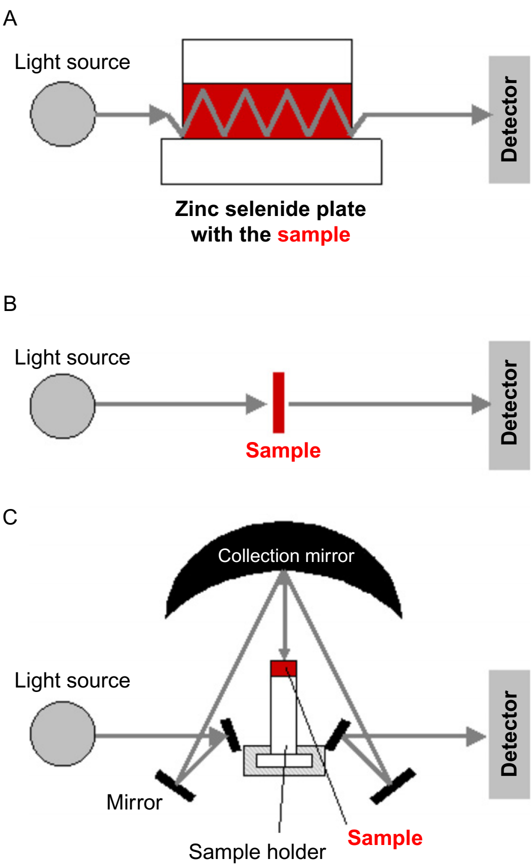


Figure 3.7 Schemes of IR light beam used in (A) attenuated total reflection (ATR), (B) KBr, and (C) DRIFT technique. *Adapted from Hesse et al. (2005).*

ground in an agate mortar. The mixture is converted into pellets by using a 9-Mg compactor, placed onto the sample holder, and analyzed by FTIR transmission technique in adsorption mode (Celi et al., 1997; Günzler and Böck, 1990) (Fig. 3.7B). The KBr technique yields highly resolved spectra that are easy to interpret; the adsorption bands of the OM functional groups are not affected by those of the KBr. However, disadvantages are that KBr technique requires mixed and finely ground samples and that acidic functional groups in organic molecules will exchange their protons by K^+ which may cause a shift of the C=O absorption bands from the region at 1700 cm^{-1} to that at 1600 cm^{-1} (Günzler and Böck, 1990).

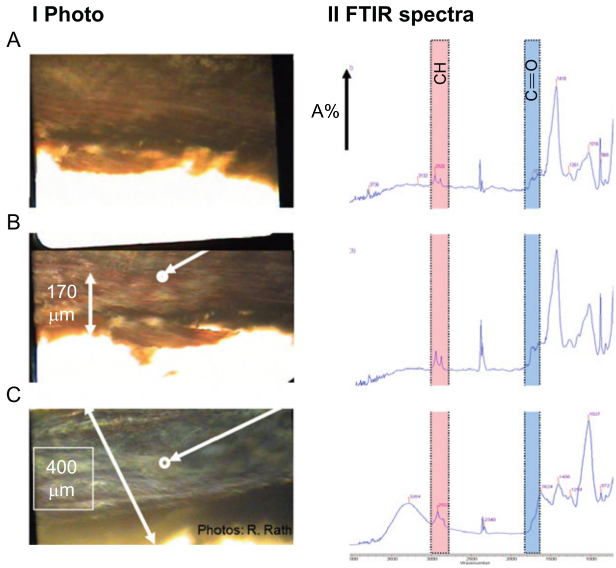


Figure 3.8 Microscopic photos (I) of different regions of a longitudinal cut of a fossil reed root sampled in a fen. Location (A) describes a darker region near the outside of the root, (B) is a region located about 170 µm inside, and (C) a region in the central part of the root. The ATR technique analyzed a region of about 20 µm in diameter, marked by a white circle. The ATR spectra (II) of the regions marked by white circles are shown at the right-hand side.

d. Combination of FTIR and a microscope: FTIR microscopy (Aparicio et al., 2002; Gregoriou and Rodman, 2002) used intact samples embedded in polyresins and thin sections allowing a spatially resolved analysis of surfaces (Mertig et al., 2002) and a spatial allocation of functional characteristics of organic components to micromorphological structures (Aparicio et al., 2002; He et al., 2002; Zieba-Palus, 1997). However, the FTIR signals of the resins may overlap with those of the OM in the sample (Arocena et al., 1995). Furthermore, the resin may interact with mineral soil components (i.e., C=O-functional groups with Ca^{2+}- or Fe^{3+}-ions) causing shifts in absorption bands that complicate the interpretation of the spectra (Aparicio et al., 2002; Dupuy and Douay, 2001). An alternative is offered by the DRIFT technique.

e. Diffusive reflectance infrared (DRIFT) technique: For DRIFT analysis, ground bulk or diluted dry soil samples are typically filled in small cups (e.g., Gottwald and Wachter, 1997). A dilution in KBr is required for analyzing OM fractions, while for bulk samples with OM contents

below about 10%, a dilution is not required (Reeves, 2003). The IR light is sent onto the plane and homogeneously prepared sample surface, and the diffusively reflected light is collected (Fig. 3.7C) and DRIFT spectra are displayed in reflectance mode. The DRIFT technique has been used as a relatively rapid technique to analyze composition and dynamics of OM in soil (e.g., Fuller and Griffiths, 1978; Niemeyer et al., 1992; Reeves et al., 2001; Spaccini et al., 2001; Tremblay and Gagne, 2002); however, DRIFT yields less highly resolved spectra as compared to the KBr technique (Haberhauer and Gerzabek, 1999). For analyses of soil samples, the advantage is that DRIFT technique is relatively easy; however, the standard procedure is applicable only to finely ground samples. The DRIFT technique combined with a horizontal positioning device could also be used for analyzing samples like plates used for thin layer chromatography (Böcker, 1997). But it has not been used for *in situ* analyses of OM composition at intact soil surfaces probably caused by problems linked to surface properties of undisturbed soil samples (uneven surfaces and contents of coarser particles). Relatively large particles, for instance, may limit the use of Kubelka–Munk (KM) transformation of DRIFT, which was developed for finely ground samples (Kortüm et al., 1963).

4.3.1 Interpretation of FTIR spectra

For characterization of OM composition, the spectra can be used to qualitatively identify OM functional groups and their relative amounts in comparable samples (e.g., CH/C=O ratios; Ellerbrock et al., 1999a, 2005). In addition, FTIR spectra displayed in absorption mode may be quantitatively evaluated to analyze the content of OM functional groups in soil samples after calibration. Such quantification is based on the relation between the height of absorption bands, that is, absorbance, A, (%) and the amount of functional groups, expressed by the law of Lambert–Beer (Eq. 3.3) as (Hesse et al., 2005):

$$A = \varepsilon c d \tag{3.4}$$

with ε, an molar extinction coefficient (mol cm^{-2}, however, in general mentioned without a dimension) that is specific for each component and each wave number, c, the molar concentration of functional group (mol l^{-1}), and d, the thickness of the sample (cm). For example, the height of the absorption band at 1750 cm^{-1} can be used to determine the amount of carboxylic acid groups if ε for the wave number and component as well as the

thickness is known (e.g., Günzler and Böck, 1990). For the quantification of spectra obtained by DRIFT technique in reflectance mode, the KM transformation has to be carried out such that band heights will be approximately linearly related to the relative amounts of functional groups (Fuller and Griffiths, 1978; Mitchell et al., 1994). Note that for determining the complete molecular structure of OM, the results from FTIR spectral analysis need to be combined with additional information on the C backbone of molecules that can be obtained by NMR, elemental analysis, and mass spectroscopy.

4.3.2 A note on PCA/PLS analysis for determining soil C_{org} contents

More recently, the DRIFT spectroscopy was combined with principal component analysis (PCA) and partial least square (PLS) analysis for the quantification of SOC contents in neat (nondiluted) ground soil samples to develop a relatively cheap method to analyze SOC contents of a large number of soil samples (e.g., Reeves, 2003). Note that the PCA/PLS method first establishes a calibrated relation between spectral data and SOC content by using PLS on a subset of the samples and second validates the relation by using the remaining data set (Ludwig et al., 2008). Like near-IR spectroscopy (e.g., Stenberg et al., 2010), the mid-IR spectroscopy (4000 to 400 cm^{-1}) discussed here could be used to assess C_{org} and N contents of soils and litter (Ludwig et al., 2008). However, the mid-IR spectroscopy offers more detailed information on OM composition since the absorption bands of functional groups like C=O and CH are less overlapping in mid-IR as compared to near-IR spectroscopy (Hesse et al., 2005). Details on PCA/PLS procedures are beyond the scope of this chapter since it contributes only little information to the analysis of SOM composition.

5. APPLYING FTIR SPECTROSCOPY IN ORGANIC CHEMISTRY AND IN SOIL SCIENCE

The above-mentioned spectroscopic techniques are generally used in chemistry as complementary methods to analyze the composition of defined OM in terms of the molecular structure. The requirement for analyzing mixtures (e.g., water and oil) for the application of the spectroscopic techniques in chemistry is that spectral signals are known and easily be distinguished, also the mixtures need to consist of maximal two or three well-known components, or the components of the mixture belong to the same substances class. The spectral methods were mainly used to detect impurities

(e.g., spots within plastic foils; Böcker, 1997) or to detect and quantify a certain component with a well-known composition within a relatively homogeneous mixture that show easily detectable signals (e.g., glucose in blood; Shen et al., 2003), or CO_2 in gases (IR detector in elemental analysis; DIN ISO 10694, 1994).

5.1. Spectral analysis of defined organic components and SOM

In contrast to defined OM substances (e.g., quinine, glucose, ascorbic acid) or substance classes (e.g., fatty acids), OM in soil and fractions is not a well-defined substance but a complex mixture of organic components (Hayes and Clapp, 2001). SOM is characterized by differing compositions, microbial degradability, and turnover time (von Lützow et al., 2006). The NMR and FTIR spectra of mixtures like SOM will give information on the *mean* functional composition. OM structures as suggested by Stevenson (Fig. 3.1) can only illustrate the mean composition of SOM.

The FTIR spectrum of glucose shows a broad absorption band at 3700–3600 cm^{-1} for the OH groups and a strong sharp absorption band at 1050 cm^{-1} for the C—O—C groups. The C—H groups—a relative small content in glucose (Fig. 3.9A)—show a hardly detectable absorption band at 2900 to 2800 cm^{-1} (pink region). Note the absorption bands of the CH groups are in general much lower than those of OH or C—O—C groups (Hesse et al., 2005).

The FTIR spectrum of glycerin (Fig. 3.9C) shows a broad and intense absorption band of the OH band and absorption bands resulting from CH groups that appear as a weak shoulder on the broad OH band, while an absorption band of a C—O—C group is missing because such groups are not part of the glycerin molecular structure. For ascorbic acid, the absorption band of the OH groups shows a fine structure due to the presence of OH groups within different molecular environments (Fig. 3.9D). Note that in case the samples contain an increasing amount of water molecules, such a fine structure will disappear (Günzler and Böck, 1990) caused by increasing inter- and intramolecular interactions via hydrogen bridging, resulting in a high variety of different molecular environments which will strongly overlap and result at the very end in one broad absorption band. In case of the dry samples, such interactions will decrease because most of the OH groups are not within a distance to form hydrogen bridges (Günzler and Böck, 1990).

In contrast to the FTIR of glucose and glycerin (Fig. 3.8A and C), the FTIR spectra of ascorbic acid (Fig. 3.9D) show an absorption band at 1750 and 1650 cm^{-1} due to C=O groups in the molecular structure (which is not

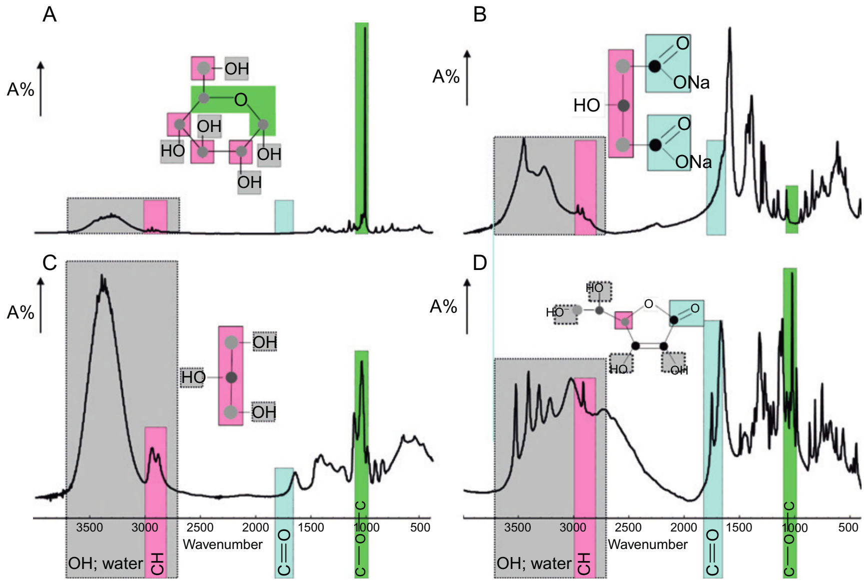


Figure 3.9 FTIR spectra of (A) glucose, (B) sodium citrate, (C) glycerin, and (D) ascorbic acid obtained with KBr technique displayed in absorption mode (A%). The marked areas indicate the absorption bands of CH—groups (pink), C=O—groups (turquoise), C—O—C—groups (green), and OH—groups (gray). The molecular structures are displayed for each substance.

part of cellulose or glycerin). The absorption band at 1750 and 1650 cm^{-1} indicates that ascorbic acid contains beside OH, CH groups and C=O groups as well. In general, the C=O groups that are part of carboxylic acid groups will show absorption bands at 1800 to 1700 cm^{-1}. However, in case the sample was mixed with KBr, a part of the protons within the carboxylic acid groups will be exchanged by K^+ and the FTIR will show the absorption bands of the deprotonated acid group at 1670 to 1640 cm^{-1} (Günzler and Böck, 1990) which is also found in FTIR spectra of sodium citrate (Fig. 3.9B).

For clay mineral components, high-resolved spectra could be obtained as well (Fig. 3.10A): The FTIR spectra of clay minerals show a high absorption band at 1100 cm^{-1} caused by Si—O—Si groups. Such absorption bands strongly overlap with those of the C—O—C groups in organic components. Additionally, the clay minerals show broad absorption bands at 3800 to 2700 cm^{-1} due to OH groups (Fig. 3.10A). In case a clay sample (e.g., kaoline) is mixed with ascorbic acid, the FTIR spectra of the mixture show absorption bands of both components (Fig. 3.10B), whereby the

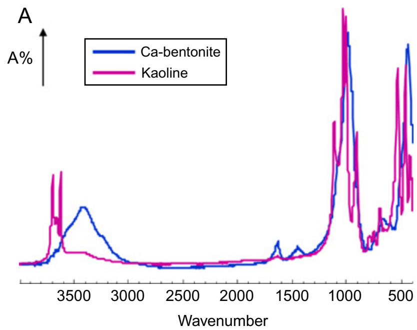


Figure 3.10 FTIR spectra of (A) Ca-bentonite and kaoline and (B) ascorbic acid (green area), kaoline (pink area), and a mixture of both (brown line) measured with KBr technique in absorption mode (A%).

intensity of the absorption bands behaves additive. The brown line in Fig. 3.10B results from the mixture and shows absorption band of both the ascorbic acid and the kaolin sample.

While the green-colored area in Fig. 3.10B is from the FTIR of ascorbic acid and the red area is from FTIR of kaoline, the brown line is the spectrum of the mixture. By using spectral subtraction procedures, the spectra of the single components can be obtained provided that at least one component of the mixture is known (Senesi et al., 2001) and the mixing did not induce any chemical reactions between the components.

FTIR spectra of mixtures (i.e., soil samples) are less resolved (Fig. 3.11) as compared to those of defined organic components like ascorbic acid (Fig. 3.9). Especially, the fine structure in FTIR spectra, often called fingerprint region (i.e., 900 to 400 cm^{-1}), is less resolved in mixtures such as soil samples (Fig. 3.11). The fingerprint region in FTIR reflects structural information on the molecular structure (i.e., status of substitution or conformation) of defined organic components as, for instance, ascorbic acid (Fig. 3.9).

The spectral data will reflect information on the mean composition of SOM or OM fractions. The examples in Fig. 3.11 show that most intense absorption band of soil samples is at a wave number of about 1100 cm^{-1} caused by Si—O—Si groups within quartz and clay minerals (Ellerbrock et al., 1999a; Gottwald and Wachter, 1997). The second most intense absorption bands can be found in the region 3800 to 2700 cm^{-1}. These bands reflect the presence of OH groups (Gottwald and Wachter, 1997) in either OM components (i.e., phenols, alcohols, carboxylic acids) or soil minerals (i.e., in clay minerals or iron or manganese hydroxides among others).

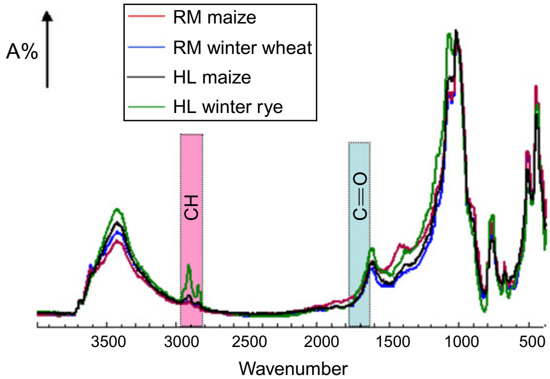


Figure 3.11 FTIR spectra of soil samples from NPK-fertilized plots at long-term field experiments located at Halle and Rotthalmünster measured with KBr technique and displayed in absorption mode (A%); more information on Halle and Rotthalmünster soils can be found in Ellerbrock and Kaiser (2005).

5.2. Applications of FTIR spectral analysis to characterize OM fractions

Although the determination of specific molecular structures of SOM is not possible, FTIR can be used to determine the relative contents of functional groups in SOM when focusing only on those absorption bands that are indicative for OM. Van der Marel and Beutelspacher (1976) found that IR spectra of humic acids from various origins (i.e., peat, coal, lignite, lignin from straw or Black Earth, Podzol, and Chernozem soils) were similar but not identical. These authors assumed that variations in IR were caused by slight differences in the composition of the samples. Hempfling et al. (1987) found by using FTIR differences in the OM composition of forest soils from different sites. They stated that during decomposition of litter, humification, and podzolization, the content of cellulose and lignin decreased, whereas hemicellulose and protein contents appeared unchanged. Land use, crop rotation, fertilization (Nardi et al., 2004), land use history (Antil et al., 2005), and soil genesis (Quideau et al., 2001) were found by using FTIR analysis to effect SOM composition as well.

To allow a more detailed spectroscopic analysis, various OM fractions have been separated from the soil to reduce or eliminate the effects of absorption bands of soil mineral components in FTIR (Janik et al., 1995) (see also sections 3.1 to 3.4 in this chapter). Effects of different site conditions on the composition of dissolved organic matter (DOM) have been reported

by Guggenberger et al. (1994a,b) for a silty loam soil from loess in a pre-Alpine region. For a clay loam, Gerzabek et al. (1997) found characteristic differences in the composition of fulvic and humic acids only for peat-amended soil, using FTIR and not for other treatments. However, Gerzabek et al. (1997) used a variation of the Nujol technique: They applied the extracts onto disposable IR cards (3 M; polyethylene), dried them, and FTIR analyzed as described for Nujol technique.

The use of OM fractions allowed to demonstrate with FTIR (KBr technique), for example, that the content of polysaccharides in DOM fractions from forest soils changed during the decomposition process (Kalbitz et al., 2003). In another example, the addition of Al to fractions of the DOM was found by FTIR analysis to cause the DOM composition in the precipitated fraction to change as compared to the DOM in solution (Scheel et al., 2008).

For agricultural soils, amount and type of OM functional groups were found to be affected by land use and management practices (e.g., Ellerbrock et al., 1999a,b, 2001a; Gerzabek et al., 1997, 2001; Kaiser et al., 2011; Quideau et al., 2001). FTIR studies on OM composition of SOM fractions from soils with the same genesis indicated effects of farm yard manure (FYM) application such as an increase in carboxyl group content (Ellerbrock et al., 1999b). Antil et al. (2005) found the same effect but for bulk soil and silt-sized fractions. Soils of LTFE (i.e., at least 30 years) listed in Table 3.3 have been used for studying changes in OM composition (e.g., Antil et al., 2005; Ellerbrock et al., 1999a,b; Gerzabek et al., 1997, 2006; Kaiser et al., 2007; Tatzber et al., 2007).

For a comparison of the FTIR spectra of the NaPY-soluble OM fraction of both loamy and sandy soil samples (Fig. 3.12), the intensity of the absorption bands at 1710 and 1690 cm^{-1} (i.e., indicating C—O groups) was highest for the plots that received FYM (Ellerbrock et al., 1999b). According to the high absorption intensities at 1710 and 1690 cm^{-1}, Ellerbrock et al. (1999b) expected relatively high CEC values for the fraction of the soil from the FYM-fertilized plots because the intensity of these absorption bands was reported to be correlated with CEC (Celi et al., 1997; Günzler and Böck, 1990). The CEC of the NaPYseq-soluble OM fraction was found between 25 and 375 $cmol_c\ kg^{-1}$, which represents a fraction between 1% and 11% of the CEC of the bulk soil (Kaiser et al., 2008).

The CH groups reflect the hydrophobic properties of OM (Morrison and Boyd, 1983) that may be related to the wettability (Capriel, 1997; Capriel et al., 1995); the relative amount of CH groups could be analyzed

Table 3.3 FTIR studies on OM composition of soils from long-term field experiments (LTFE) and applied FTIR techniques

Location	Country	Established in	Texture	References on LTFE	References on FTIR spectra	OM fractions	FTIR technique
Müncheberg	Germany	1963	Sandy loam	Körschens and Müller (1996)	Ellerbrock et al. (1999a,b)	NaPY soluble	KBr
Dedelow		1976	Sandy loam	Körschens and Müller (1996)	Ellerbrock et al. (1999b)	NaPY soluble	KBr
Groß Kreutz		1967	Sandy loam	Körschens and Müller (1996)		NaPY soluble	KBr
Halle		1887	Loamy sand	Merbach et al. (1999)	Kaiser et al. (2007)	NaPYseq soluble, water soluble	KBr
Bad Lauchstädt		1902	Silty loam	Körschens and Müller (1996)	Kaiser et al. (2007)	NaPYseq soluble, water soluble	KBr
Rotthalmünster		1969	Loamy silt		Ellerbrock and Kaiser (2005)	NaPYseq soluble, water soluble	KBr
Broadbalk	UK	1843	Loamy silt			NaPY soluble	KBr
Ultuna	Sweden	1956	Silty clay (37% clay; 41% silt)	Kirchmann et al. (1994)	Gerzabek et al. (1997)	NaPY soluble	Nujol-like technique
					Gerzabek et al. (2006)	Bulk soil, silt-size fraction	KBr
					Tatzber et al. (2007)	Soluble OM fractions	KBr

Prague-Ruzyne	Czech Republic	1955	Clay loam	Skarda and Jokesova (1982)	Filip and Kubát (2001), Simon (2007)	Humic acid, bulk soil	KBr
Gumpenstein	Austria	1962	Silt loam		Antil et al. (2005)	Particle-size fractions	KBr
Lower Austria	Austria		Loamy silt	Spiegel et al. (2002)	Tatzber et al. (2006)	Bulk soil, humic acid	KBr
Several sites	Brazil	–			Madari et al. (2006)	Bulk soil, particle-size fraction	DRIFT for C content

The analyses were carried out for SOM (bulk soil), particle-size fractions, water soluble, sodium pyrophosphate soluble (NaPY), and sequentially separated sodium pyrophosphate-soluble (NaPYseq) OM fractions.

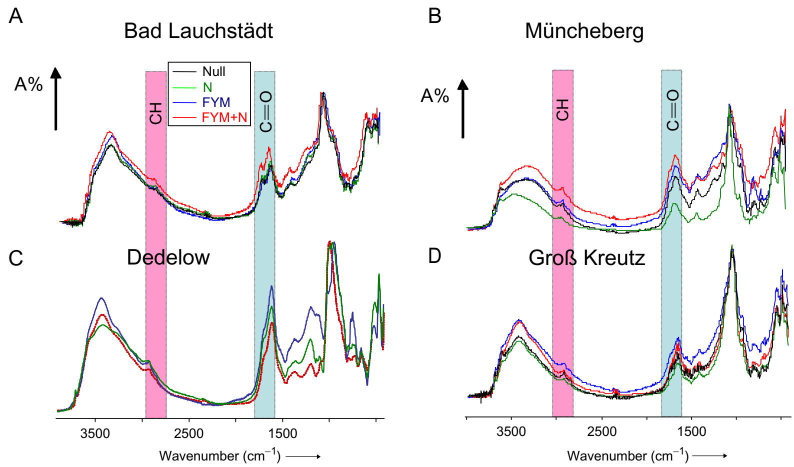


Figure 3.12 FTIR spectra of the sodium pyrophosphate-soluble OM fraction from soils of differently fertilized plots (Null, no fertilizer; N, mineral nitrogen; FYM, farm yard manure; FYM+N, farm yard manure plus nitrogen) of long-term field experiments located at (A) Bad Lauchstädt, (B) Müncheberg (Ellerbrock et al., 1999b), (C) Dedelow (Ellerbrock et al., 2001a,b), and (D) Groß Kreutz. The spectra were measured with KBr technique and displayed in absorption mode (A%) have been corrected with the spectra of the mineral phase (Ellerbrock and Gerke, 2004).

from the intensity of the absorption bands at 2800 and 2950 cm^{-1}. For example, the bands in the spectra representing CH groups are higher for samples from sandy (Fig. 3.12D) as compared to those of a loamy soil (Fig. 3.12A) from plots with similar FYM application (Ellerbrock et al., 2001a,b).

However, the information on the composition of SOM fractions are limited due to artifacts caused by separation procedures (e.g., Hayes, 1985), especially in case sodium hydroxide solution is used (Kononova, 1958), and speciation caused by the solubility of SOM according interactions with mineral surfaces (Piccolo et al., 1993) depending on type of cations (e.g., Ca^{2+}, Al^{x+}, Mn^{x+}, or Fe^{x+}) and amount of clay (Mikutta et al., 2005b) during extraction.

6. RELATIONS BETWEEN SOM COMPOSITION AND SOIL PROPERTIES

It is well known that content and composition of clay minerals and SOM determine the physicochemical nature of soil (Stevenson, 1994) including wettability (e.g., Dekker and Ritsema, 1994) and CEC

(Sposito, 2008). Thus, differences in SOM composition affect soil properties in a similar way as differences in clay mineral composition (e.g., Gerzabek et al., 2001). SOM content and composition are especially important for sandy soils with low clay mineral content, where SOM acts as the major sorption partner for cations (e.g., Almendros, 1995; Hepper et al., 2006). Determination of SOM composition can therefore improve predictions on changes in soil properties as affected by long-term soil management or changes in land use.

6.1. CEC and SOM composition

The CEC of soils characterizes sorption properties that are important, for instance, for describing nutrient retention and supply or the fate of heavy metals and pesticides (e.g., Leinweber et al., 1993). In arable top soils of temperate regions, the CEC is determined mainly by negatively charged sites of (i) 2:1 clay minerals with either permanent (e.g., smectite; Mendonça and Rowell, 1996) or variable charge (e.g., metal oxides; Oorts et al., 2003; Parfitt et al., 1995) and (ii) dissociated carboxyl groups of humic acids (Coles and Yong, 2006; Martyniuk and Więckowska, 2003). The abundance of negatively charged sites depends on (i) the mineral composition of the parent rock and sediments, (ii) mineral weathering processes (Hepper et al., 2006; Oorts et al., 2003), and (iii) pH-dependent structure of SOM (Asadu et al., 1997; Coles and Yong, 2006). The formation of organo-mineral complexes (OMC) may modify the CEC of SOM and clay minerals in soils (Oades, 1989) as follows: The CEC of clays coated with OM can differ significantly from that of uncoated clay minerals (Dudas and Pawluk, 1970; Kahle et al., 2002). Thompson et al. (1989) found the CEC of OMC to be mostly lower than the sum of the CEC values from both organic and inorganic components. The CEC values of soils vary widely depending on the amount and composition of clay minerals and SOM (Kyziol et al., 2006; Parfitt et al., 1995). The relative importance of SOM for the CEC of the soil increases with decreasing amounts of negatively charged 2:1 clays (Hepper et al., 2006). The CEC of SOM is mainly related to the content of carboxyl groups (Barančíková et al., 1997; Coles and Yong, 2006), which can be quantified with FTIR spectroscopy (Celi et al., 1997).

In previous studies, CEC of OMC was analyzed (e.g., Hepper et al., 2006; Leinweber et al., 1993; Oorts et al., 2003). Such complexes were separated from soil using aggregate and particle-size fractionation techniques including density separation, sieving, and ultrasonic treatment. However,

the CEC of such OMC reflects the CEC of both the OM and the minerals. For analyzing CEC of OM fractions, those fractions need to be separated themselves (i.e., without complexation with minerals). A possibility was offered by studies that determine sorption properties of OM fractions like humic acids from the content of carboxyl group analyzed with FTIR (Barančínková et al., 1997; Celi et al., 1997; Coles and Yong, 2006), among other techniques. Still, the knowledge on the relation between CEC and OM composition is limited, partly because SOM separation techniques are not suitable. For loamy and sandy soils from two LTFE, between 13% and 34% of SOC could be extracted sequentially with NaPY. The composition of this OM fraction (i.e., the content of carboxyl groups) was used to identify long-term effects of crop rotation and fertilizer application by using FTIR (Kaiser et al., 2007).

For the soils from the same LTFE, the contribution of NaPYseq-soluble OM fraction to CEC(soil) was determined by comparing the chemical composition of SOM with that of the OM fraction. The experiments at Halle (HL) and at Bad Lauchstädt (BL) were selected because of their similar age (i.e., about 100 years) and soil pedogenesis (i.e., loam derived from loess). The CEC of NaPYseq-soluble OM was determined by using a slightly modified procedure as described by Leinweber et al. (1993). To simulate an SOM content of 3% in soil (which is nearly 1.5% SOC), Kaiser et al. (2008) used a mixture of 0.03 g of freeze-dried NaPYseq-soluble OM fraction and 4.97 g of acid-purified sand (Seesand, Carl Roth, Karlsruhe, Germany): This mixture was added to a 50-mL glass beaker and stirred with a glass stick for about 2 min until the mixture was uniformly colored. This mixture was then placed in a percolation tube and the CEC was determined according to DIN 19684 (1977). The Ba^{2+} concentration in the combined percolates was determined using an atomic absorption spectrometer (1100B, PerkinElmer, Waltham, MA) to yield the CEC of the NaPYseq-soluble OM in terms of charge equivalents (Kaiser et al., 2008).

The CEC of the NaPYseq-soluble OM fraction per unit mass of soil was found to depend on amount and composition of this OM fraction. The relation between the intensity ratio of absorption bands of the CO and COC groups (CO/COC) for the *per unit mass of OM* and the CEC of the NaPYseq-soluble OM fraction was found to be relatively linear even including the soils of the FYM plots (Fig. 3.13). A similar relation between CO/COC ratios of an NaPYseq-soluble OM fraction and the CEC(PY) has been reported by Kaiser et al. (2008), although sequentially extracted and soils had

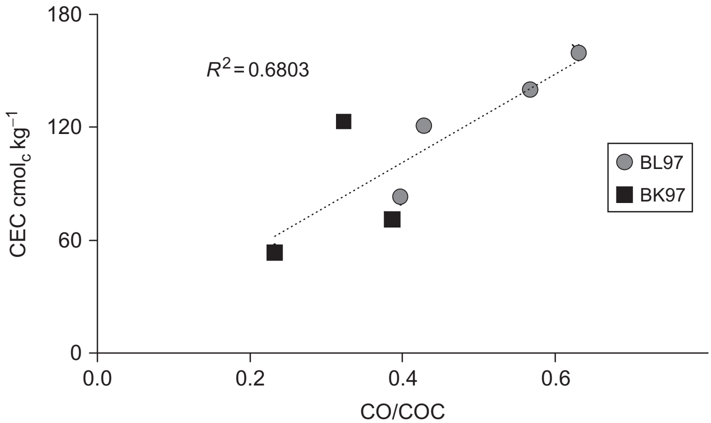


Figure 3.13 Cation exchange capacity (CEC) per unit mass of OM versus the ratio of the intensity of absorption bands of the C=O and the C—O—C groups in FTIR (CO/COC ratio) for the NaPYseq-soluble OM fractions from soil samples of long-term field experiments at Bad Lauchstädt (BL) and Broadbalk (BK). *Modified from Ellerbrock et al. (2001a,b)*

higher clay contents as those reported in Ellerbrock et al. (2001a,b). The linear relationship of the form

$$CEC = 159.3 CO/COC \quad (3.5)$$

determined by Kaiser et al. (2008) indicates that for the NaPYseq-soluble OM, the carboxyl group content is similarly related to the CEC, as theoretically expected for pure organic compounds (Günzler and Böck, 1990).

The relation between the CEC and the relative carboxyl group content (CO/COC ratio) in the NaPYseq-soluble OM (Kaiser et al., 2008) confirms that the composition determines the sorption properties of OM. However, the limited extractability of the NaPYseq-soluble OM fraction (i.e., also depending on soil mineral and OM composition) still limits transfer of conclusions to the bulk SOM. Note that the extraction procedure may have affected the number of available sorption sites, since the complexation by pyrophosphate removes adsorbed minerals that were originally interacting with the NaPYseq-soluble OM fraction in soil.

6.2. Wettability of soils and SOM composition

Wettability is the ability of a liquid (e.g., water) to spread on a solid surface (Letey, 1969) and related to the solid–liquid contact angle (CA), which depends on the solid surface free energy and the surface tension of the liquid; the CA is determined at the air–water–solid boundary line (Letey, 1969).

Values of the CA between 0° and 90° indicate a subcritical (i.e., not hydrophobic) range of water repellence; values >90° indicate a water-repellent porous medium (Morrow, 1976; Siebold et al., 1997).

Attempts to explain soil water repellency focused on the SOM content (e.g., Chenu et al., 2000). These attempts assumed that the SOM provides a large number of hydrophobic components such as aliphatic constituents (Capriel, 1997; DeBano, 1981) and waxes (Franco et al., 2000). In comparison to the SOM content, the OM composition allowed a better prediction of soil water repellence (McKissock et al., 2003). When using the intensity of the absorption bands of the CH groups in FTIR spectra (i.e., wave numbers 2950 and 2800 cm^{-1}), Capriel et al. (1995) estimated a potential wettability and McKissock et al. (2003) tried to relate spectral information to the wettability determined with water drop penetration time tests. However, conflicting results were found by Mataix-Solera and Doerr (2004) and Horne and McIntosh (2000). Negre et al. (2002) suggested that wettability may be better explained by a combined effect of hydrophobic and hydrophilic groups in OM as already stated by Morrison and Boyd (1983) for defined OM. For example, fatty acids, which contain both COOH and CH groups, change from hydrophilic to hydrophobic character if the carbon backbone consists of more than five C atoms (Falbe and Regitz, 1998).

To prove if the ratio between hydrophobic and hydrophilic groups in OM could be used to improve the description of soil wettability, Ellerbrock et al. (2005) determined the ratio by FTIR analysis by using the intensity of the CH bands as a measure for the hydrophobic (A) and the intensity of the CO bands as a measure for the hydrophilic groups (B) and related the obtained CH/CO ratio with the wettability of soil samples. For soils with SOC contents below about 10 g kg^{-1}, the wettability was found to increase with SOC content, while for soils with SOC contents larger than 10 g kg^{-1}, it was found to decrease (Fig. 3.14).

The CA was expected to increase with larger values of the CH/CO ratio since the content of hydrophobic relative to hydrophilic groups increases in that case. When plotting CA versus the CH/CO ratio determined with FTIR for the SOM of bulk soil samples (Fig. 3.14B), the data follow the expected relation except for the samples of the Podzol site. Note that the CH/CO ratio only reflects the mean composition of the OM in the bulk soil, and it did not yield information on interactions between OM and soil minerals or the ratio between OM content and soil mineral surface.

In principle, SOM is adsorbed onto mineral surfaces via PC such as Ca^{2+}, Al^{x+}, Mn^{x+}, or Fe^{x+}. Therefore, both SOM and mineral composition and

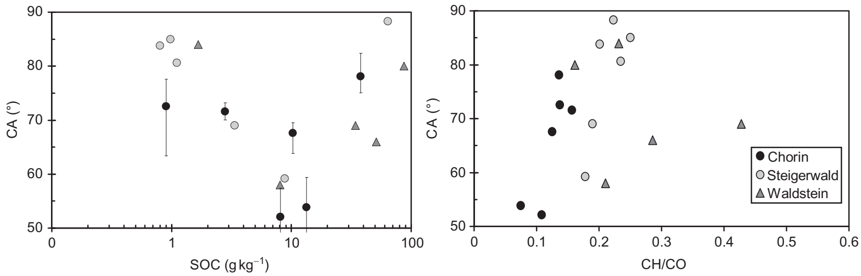


Figure 3.14 Contact angles (CA) related to (A) C_{org} contents and (B) the ratio between hydrophobic C—H and hydrophilic C═O groups (CH/CO ratio) determined by FTIR for bulk forest soil samples from the sites at Chorin, Steigerwald, and Waldstein. *Adapted from Ellerbrock et al. (2005).*

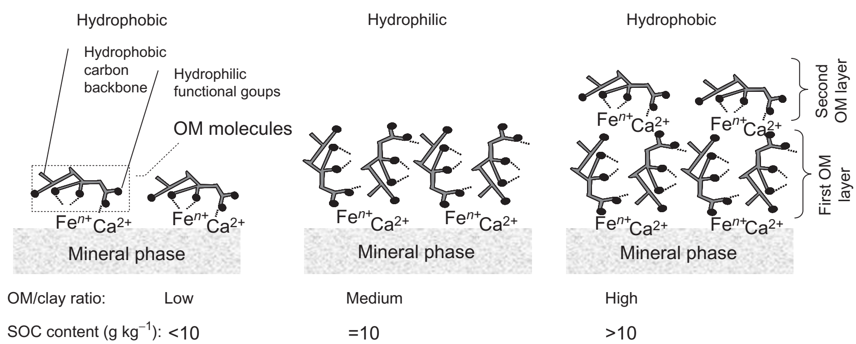


Figure 3.15 Schematic illustration of possible spatial orientations of organic matter (OM), consisting of the carbon backbone chains (solid gray) and the functional groups (solid black circles) toward the mineral surface depending on the relations between the number of OM molecules at the mineral surfaces and the OM/mineral ratio, that is, the ratio between OM and clay content (Ellerbrock et al., 2005).

the presence of PC, may determine the "effectiveness" of SOM to affect soil wettability: In case of a relatively low OM/mineral ratio, all hydrophilic groups of the OM molecules can adsorb to the mineral surface resulting in a sparse flat "monolayer" of SOC (i.e., a single layer of OM molecules) whereby most hydrophobic groups are directed toward the outer surface (Ellerbrock et al., 2005) (Fig. 3.15A). Under such conditions, the hydrophobic groups of SOM are more effective with respect to soil wettability than the mean OM composition (CH/CO ratio) determined by FTIR may suggest.

Depending on the OM/mineral ratio, the spatial orientation of the OM molecules in that layer will change from a sparse flat (i.e., "low," Fig. 3.15,

left) to a dense upright one (i.e., "medium," Fig. 3.15, center) (Clapp et al., 2001).

In case of a "medium" OM/mineral ratio, a maximum amount of OM molecules forms a "monolayer" at the mineral surface (Fig. 3.15, center, now in a dense upright orientation) such that, both, hydrophilic and hydrophobic, components will appear at the outer surface. Thus for a "medium" OM/mineral ratio, soil wettability can be expected to correspond with the CH/CO ratios determined by FTIR. In case of larger OM/mineral ratios (Fig. 3.15, right), the outside surface of the "monolayer" can interact with a "surplus" OM molecules if PC are present, while forming a second layer. The outer surface again becomes more hydrophobic initially since the hydrophilic functional groups again tend toward the inside and the hydrophobic ones toward the outside. With further increasing OM content—forming onion-like structures (e.g., Kleber et al., 2007), more hydrophilic groups may again be directed toward the outside. Thus, the effectiveness of OM composition with respect to soil wettability needs to be weighted at least with respect to the OM/mineral ratio. In order to evaluate the effectiveness of CH/CO ratio, Ellerbrock et al. (2005) introduced an optimized, none-dimensional weighing factor as a function of the SOC/clay ratio (g g^{-1}).

In fact, the effectiveness factor improved also strongly the relation between CAs and the weighted CH/CO ratios for bulk soil OM (Fig. 3.16A). The results suggest that such effectiveness factor may well be described with an exponential relation. For describing the relation between wettability and the CH/CO ratio measured for the NaPYseq-soluble OM fractions, site-specific coefficients were required (Ellerbrock et al., 2005). This could be explained by differences in soil genesis, which are manifested in the content of PC within the soil, and in site-specific compositions of inorganic compounds (i.e., clay minerals, Fe, and Mn oxides).

7. FROM THE LAB TO THE FIELD

7.1. Modifications by soil sampling of structured soils

The characterization of SOM and OM fractions using FTIR spectra has in the majority of the before-mentioned studies been carried out with homogenized or otherwise intensively mixed samples collected mostly from the topsoil horizon. Mixing of collected soil samples can be useful where local-scale heterogeneity effects are of minor interest. The results obtained from spectroscopic analysis of mixed samples can be used, for example, for

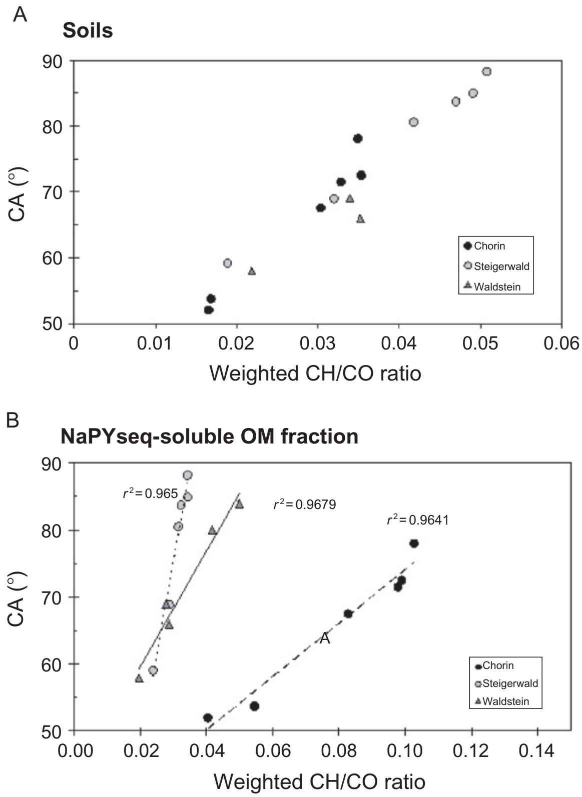


Figure 3.16 Contact angles (CA) related to the weighted ratio between hydrophobic to hydrophilic groups (CH/CO) from FTIR spectra of (A) bulk soil and (B) NaPYseq-soluble OM fractions; samples were from Chorin, Steigerwald, and Waldstein sites (Ellerbrock et al., 2005).

comparing long-term mean OM compositions that develop in an intensively cultivated topsoil of differently managed plots (e.g., Kaiser et al., 2007; Powlson, 1996).

In structured and macroporous soils, however, the local-scale spatial distribution of SOM can be especially important during preferential flow and transport of solutes in the larger and vertically continuous pore space (e.g., see reviews by Köhne et al., 2009a,b). Macropore wall coatings were reported to significantly affect especially the reactive transport in structured soil (Bundt et al., 2001; Eich-Greatorex and Strand, 2006; Mallawatantri et al., 1996). However, when mixing aggregated soil samples, the contribution of the coating will be largely lost (i.e., considering its relatively small mass fraction) and the mixture will mainly reflect the properties of the bulk

soil matrix (e.g., Bachmann et al., 2008; Horn and Smucker, 2005; Santos et al., 1997).

Recent attempts to describe flow and reactive transport in structured soil (e.g., Gerke, 2006; Jarvis, 2007) that were based on the determination of local geometry of the macropore space (Luo et al., 2010; Mooney and Morris, 2008; Ngom et al., 2011; Perret et al., 1999; Tippkotter et al., 2009) and the chemical composition of the pore surfaces (e.g., Elyeznasni et al., 2012; Kodesova et al., 2008; Köhne et al., 2011; Leue et al., 2010; Rasa et al., 2012) indicate that sorption parameters from mixed samples are not suitable for such analyses in structured soil.

Soil structural surfaces, such as clay-organic coatings on aggregate surfaces, occur, in particular, in illuvial soil horizons such as Bt horizons of Alfisols as a result of particle migration (e.g., Bronnikova et al., 2000). For biopores, functional domains (Lavelle, 2002) have been introduced to distinguish the regions close to these pores from the bulk soil matrix, such as "drilosphere" for earthworm burrows (e.g., Schrader et al., 2007) and "rhizosphere" for the environment of roots (e.g., Hinsinger et al., 2009). Furthermore, walls of worm burrows can be covered by worm feces or casts (e.g., Capowiez et al., 2011; Piron et al., 2012), abandoned burrows can be penetrated by plant roots (e.g., Leue et al., 2010), and the surface of decayed root channels may contain residues of the partly decomposed or remnant roots (e.g., White and Kirkegaard, 2010) or hydrophobic substances (e.g., Bengough, 2012). These surfaces can be different in texture, clay mineralogy, and SOM from the bulk soil matrix (Gerin et al., 2003; Guggenberger et al., 1996; Kaiser and Wilcke, 1996). In contrast to organic coatings of individual particles (Amelung et al., 2002), a coated surface of preferential flow paths is a porous medium itself. Coatings of soil aggregates or linings along biopore walls (Ellerbrock et al., 2009) may differ not only with respect to SOM contents but also to the mean OM composition as compared to the soil matrix (Ellerbrock and Gerke, 2004). The clay mineralogical composition of the coating was spatially variable at the local scale (e.g., Jongmans et al., 1998).

Since sorption properties are related to OM content and composition of coatings, the information may help characterizing effective parameters in mass exchange terms of two-domain models (e.g., Gerke, 2006). While the mineral components of aggregate coatings have previously been studied (e.g., Jongmans et al., 1998; Kaiser and Wilcke, 1996), the quantification of OM composition and physicochemical properties directly at aggregate surfaces is still limited. Previous studies (Ellerbrock and Gerke, 2004) were still

based on manually removing of a thin layer of coating material about 1 mm from soil aggregate samples and using transmission FTIR with KBr technique. Still, the intact outermost surface (i.e., the interface between matrix and flow path) of soil aggregates or biopores was not analyzed. This interface cannot be separated from the aggregates or biopores in a nondestructive way. Thus, a nondestructive method was required to measure the OM composition at the intact surface. Also, techniques such as density fractionation could not be applied because the original spatial conformation of OM functional groups as in intact soil could not be preserved in density-separated SOM fractions (see Fig. 3.3). To consider the small-scale spatial distribution of SOM in soil at flow path surfaces, a direct analysis at intact surfaces seems to be essential.

7.2. Analyzing soil structural surfaces—Transect and map

A number of spectroscopic methods and techniques are currently available for studying and visualizing the mineral and OM composition of biogeochemical interfaces in soil at the submicrometer scale (Rennert et al., 2012), including X-ray spectromicroscopy, nanoscale secondary ion mass spectrometry, atomic force microscopy, micro-X-ray tomography, and positron emission tomography. Combining the techniques is still a great challenge. However, for the analysis of soil structural surfaces (i.e., surfaces of soil aggregates and biopores), a macroscopic scale characterization of the OM composition requires the information of the properties at the millimeter scale when dealing with preferential flow in macropores.

Depending on the spatial resolution of the instrument, the "effective" properties integrated over the IR beam region were determined using DRIFT spectroscopy in different applications. The local differences in the SOM composition at the surface of soil samples could be determined by stepwise moving the sample along millimeter-scale transects while taking DRIFT spectra (Ellerbrock et al., 2009). These DRIFT transects yielded useful spectra from surfaces of disturbed soil samples as well as from intact aggregates with a relatively smooth and fine-textured surface. Ellerbrock et al. (2009) and Leue et al. (2010; 2011) combined the DRIFT technique with a positioning table to obtain millimeter-scale maps of SOM composition at intact soil structural surfaces. As for the FTIR spectra, the interpretation of these KM-transformed DRIFT spectra (Ellerbrock et al., 2009) focused on the alkyl (CH) and the carboxyl (C=O) absorption bands to characterize hydrophobic and hydrophilic functional groups in OM (Fig. 3.17). The ratio between the intensities of the CH and C=O

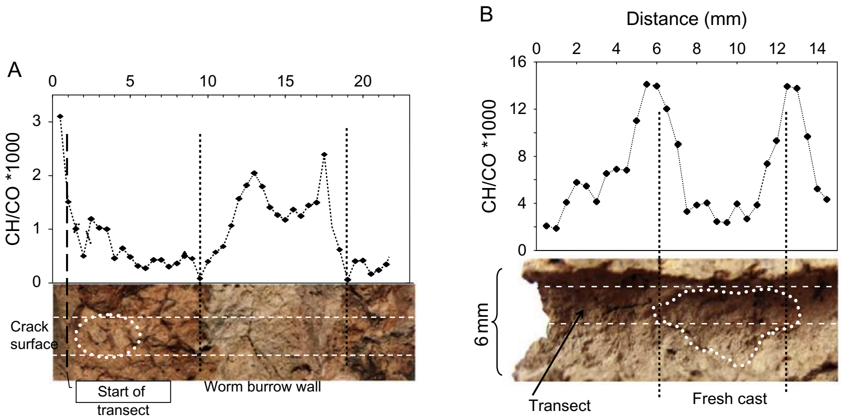


Figure 3.17 Ratios of hydrophobic to hydrophilic groups (CH/CO) ratios measured with DRIFT mapping technique along (A) a 22.5-mm transect at a soil aggregate surface perpendicular to an earthworm burrow and (B) a 14.5-mm transect within an earthworm burrow from an arable subsoil (40–80 cm depth). The vertical black dotted lines (at 9.5 and 19 mm distance) in (A) are used to mark the edges of the worm burrow. *Adapted from Ellerbrock et al. (2009)*

absorption bands (CH/C=O ratio) indicating a potential water repellency of the OM at the surface could then be analyzed in relation to their spatial distribution at the crack surfaces or earthworm burrow walls. By comparing the spectral data with photos of the corresponding sample surfaces, Ellerbrock et al. (2009) attempted a qualitative interpretation of the local distribution of clay or worm casts. The CH/C=O ratios allowed determining the position of root residues and earthworm channels along measurement transects at fine-textured surfaces of the macropores that could potentially act as preferential flow paths.

In order to analyze the two-dimensional local distribution of OM composition at intact aggregate surfaces and earthworm burrows, Leue et al. (2010; 2011) used a DRIFT mapping procedure. Examples of the millimeter-scale maps of OM composition in form of the CH/C=O ratios could be obtained for a number of intact structures from the Bt horizon of a Luvisol (Fig. 3.18). The results of DRIFT mapping indicated that the intact surfaces of aggregate samples could be grouped into regions of earthworm burrows, root channels, and aggregate coatings that were clearly distinguishable (Leue et al., 2010). Among these groups of surfaces, the potential hydrophobicity (i.e., CH/C=O ratio) was mostly higher for worm burrows as compared to aggregate surfaces or root channels (Fig. 3.19).

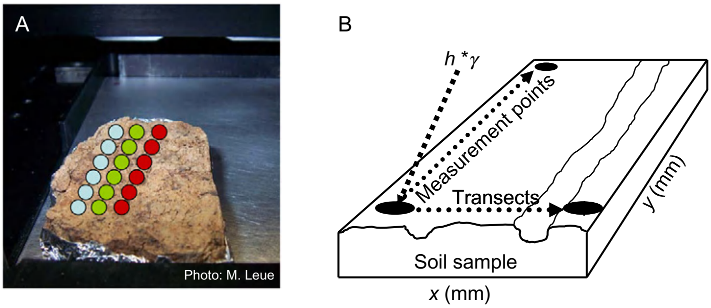


Figure 3.18 Illustration of the DRIFT mapping technique (A) photo of the positioning table with a soil aggregate sample, differently colored circles indicate DRIFT measurement points at the intact aggregate surface and (B) schematic illustration of a measurement transect along a soil structural surface.

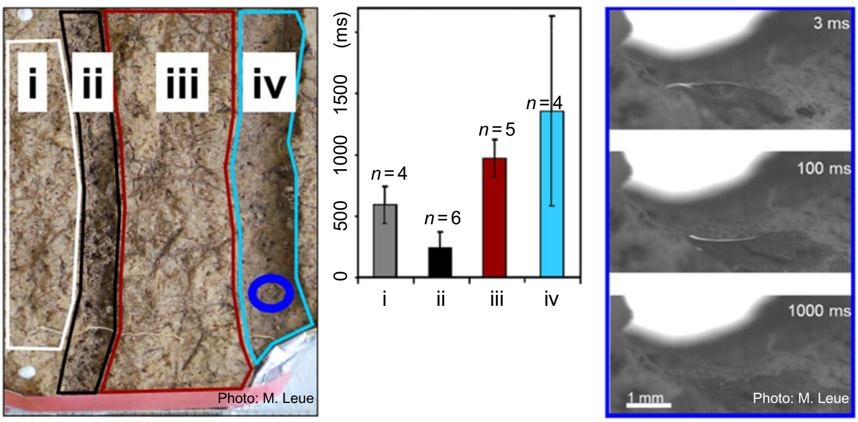


Figure 3.19 (A) Photo with marked regions at a soil structural surface, (B) water droplet infiltration times (mean values and standard deviations) measured at these regions, and (C) photos of the time-dependent contours of a water droplet placed at area *d* (i.e., at the blue circle in the left photo A). The regions indicate the left crack surface (i), an older earthworm burrow (ii), the central crack surface (iii), and a younger earthworm burrow (iv). *Adapted from Leue et al. (2010).*

Combined water drop infiltration tests (Leue et al., 2010) indicated that the infiltration was slowest for regions with a high DRIFT-measured potential wettability, such as younger worm burrow surface; infiltration was rapid for uncoated crack surfaces that had a low CH/C=O ratio. For the older worm burrow wall, the infiltration times were relatively short despite a relatively higher CH/C=O ratio (Fig. 3.19). Of course, water infiltration

depended, in addition to the CH/C═O ratio, also on the pore size and porosity of the burrow wall, which was found to be larger for older as compared to the younger burrow.

The results obtained by DRIFT mapping indicate that coatings at macropore and flow path surfaces differed locally in terms of OM composition, distribution, and possibly also in wettability, indicating yet unknown implications for preferential movement of water and reactive solutes. For more closely linking CH/C═O ratios with water infiltration, additional studies are required to determine (i) a factor that describes the effectiveness of OM composition for wettability depending on the ratio between OM and mineral (Ellerbrock et al., 2005), (ii) a spatial allocation of droplet and DRIFT measurement positions, and (iii) a spatial interpolation of the CH/C═O ratio across the droplet-affected areas. Finally, the analyses of the spectral information need to be refined to allow for a more quantitative interpretation.

8. SUMMARY AND CONCLUSIONS

This overview revealed the importance of characterizing both the content and composition of SOM. The SOM composition could be analyzed by using spectroscopic techniques like NMR and FTIR. Both techniques are in principle complementary and based on the same physicochemical principle, which is the interaction between electromagnetic radiation and submolecular components. The difference in the interactions is caused by the wavelengths of electromagnetic radiation that are used: FTIR spectroscopy is based on light of wavelength between 2.5 and 25 μm that interact with molecular bonds; NMR spectroscopy is based on the interaction between radio waves and the orientation of nuclear magnetic spins of atoms (i.e., ^{13}C and ^{1}H isotopes) in an external magnetic field. Both FTIR and ^{13}C NMR spectra provide information on SOM composition in terms of functional groups like CH or C═O groups. The NMR spectroscopy can be limited by the presence of paramagnetic elements like iron in soil. In comparison to NMR, the FTIR spectroscopy is a relatively fast technique for analyzing solid samples. FTIR provides information on the composition of organic and mineral soil components.

Effects of climate, soil genesis, land management, and land use history on SOM composition could be analyzed with FTIR spectroscopy. Although developed for finely ground and diluted samples, the DRIFT technique was found applicable to undiluted soil samples when focusing the

interpretation on specific OM absorption bands not overlapped by mineral absorption bands.

FTIR-based OM composition suggested a linear relation between the content of carboxyl groups and the CEC for a sequentially extracted OM fraction. This relation confirmed that the OM composition determines the CEC of SOM and thus also of the bulk soil. Similarly, the ratio between hydrophobic and hydrophilic functional groups determines a potential wettability of SOM and the bulk soil. Land use, SOM composition, and soil properties are, of course, interrelated. Because of this interrelation, changes in OM composition should be considered when predicting transport processes in soil and landscapes.

The transport parameters relevant for structured soils require information of the properties of potential flow path surfaces such as aggregate and biopore surfaces that are in direct contact with the percolating solute. The spatial distribution of OM composition at structural surfaces needs to be considered for adequate transport descriptions. With a DRIFT mapping procedure, millimeter-scale distributions of OM composition at intact structural surfaces could be obtained. At these surfaces, regions of higher and lower potential wettability could be distinguished.

Comparisons of OM composition and water infiltration seem promising for the aim of relating spectral information to soil properties. The mapping technique still requires further developments for considering effects of irregularly shaped surfaces on the IR light scattering. Here, the DRIFT mapping data need to be corrected for the effects of the surface geometry on the spectral intensity. The time-dependent changes in SOM composition and spatial heterogeneity effects are still widely unknown.

The presented techniques using FTIR spectroscopy allow analyzing intact sample surfaces in defined limits (i.e., relatively smooth and fine-textured surfaces). The spectra contain also information on soil mineral components not yet analyzed. Further developments and more quantitative interpretation of spectra may help improving the understanding of small-scale differences in SOM distributions and local-scale properties when studying flow and transport structured soils. The present work may provide the physical and chemical basis for application and interpretation of spectroscopic methods to structured soil.

ACKNOWLEDGMENTS

We are grateful to the Deutsche Forschungsgemeinschaft, Bonn (DFG), that provided funding for research projects (grants EL 191/5-1, and EL 191/7-1). We thank the former

PhD students Dr. Michael Kaiser and Dr. Martin Leue for valuable discussion, Prof. Dr. Radka Kodesova (University of Prague) for support with sampling and thin sections, and our cooperation partners within the DFG priority program SPP 1090: "Soils as sources and sinks for CO_2—mechanisms of organic matter stabilization," in particular, Prof. Dr. Jörg Bachmann (University of Hannover), Prof. Dr. Karsten Kalbitz (University of Amsterdam), Prof. Dr. Heiner Flessa (vTI Braunschweig), and Prof. Dr. Pieter Grootes (University of Kiel).

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CHAPTER FOUR

The Chemistry and Biochemistry of Organic Components in the Soil Solutions of Wheat Rhizospheres

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Contents

Advances in Agronomy, Volume 121
ISSN 0065-2113
http://dx.doi.org/10.1016/B978-0-12-407685-3.00004-9

Abstract

As very little is known about the chemical identities of organic compounds present in soil solutions, the purpose of this research was to chemically characterize soil solutions obtained from a Brunisol on which wheat (*Triticum aestivum*) was grown to maturity. Soil solutions were obtained by high-speed centrifugation from the rhizospheres at four growth stages of wheat: four leaves unfolded, flag leaf, grain—early milk, and grain—dry seed. Pyrolysis-field ionization mass spectrometry (Py-FIMS) was used to chemically characterize the soil solutions. We identified 346 organic components in each soil solution, which we grouped into the following 11 compound classes: carbohydrates, amino acids, phenols + lignin monomers, lignin dimers, *n*-alkyl benzenes, flavonoids, alkyl radicals, fatty acids + alkanes, N-heterocyclics + other N-compounds, sterols and steroids, and esters of suberin. The most abundant classes were lipids (fatty acids and alkanes), N-heterocyclics, and phenols + lignin monomers and dimers. The highest content of most organic components (except carbohydrates) in soil solutions occurred at the flag leaf stage of wheat growth. Many of the identified organics in soil solutions are secondary plant metabolites which represent key weapons in the continuous struggle of plant and soil microorganisms for ensuring vital space and access to nutrients and energy resources. Some of the identified compounds are also chemical signals for the interactions between plants and soil microorganisms. The chemical components of the four soil solutions from wheat rhizosphere resembled that of humic substances (HSs). Organic components in soil solutions are substrates for the microbial and chemical synthesis of HS.

1. INTRODUCTION

According to the Glossary of Soil Science Terms (1987), as quoted by Sparks (1995), the soil solution is defined as the aqueous liquid phase of the soil and its solutes which may be inorganic and organic. The majority of solutes in the soil solution are ions which occur either in free hydrated forms or as complexes with organic or inorganic ligands (Sparks, 1995). The latter author lists the total ion composition of soil solutions from world soils. The dominant metal ions are Ca, Mg, K, Na, NH_4, Al, and Si, while the ligands are HCO_3, SO_4, Cl, and NO_3.

Soil solutions are reactive media where chemical, biochemical, and physicochemical reactions occur (Monreal and McGill, 1989a). In addition, the

soil solution also contains plant root exudates, microbial metabolites, and remains of microbial cells. Microorganisms and plants can remove ions and organic compounds from the soil solution, and after their death, the organic matter is released to the soil and also to the soil solution. In the rhizosphere, the soluble organics serve as metal chelators (Marschner, 1995), plant nutrient sources (Monreal and McGill, 1989b), and allelochemicals signaling plant defense and responses to abiotic stresses (Bais et al., 2006; Weston et al., 2012).

While a considerable amount of information on the chemistry of inorganics is available in the literature, very little is known about organic compounds in the soil solution. A reason for this lack of knowledge may be the unavailability of suitable analytical methods for the identification of complex mixtures of organic components in soil solutions. Many of these components may occur in low concentrations in mixtures of hundreds of components which defy identification by most analytical methods currently available. Most existing methods have focused on the analysis of single classes of organic compounds such as carbohydrates, amino acids, and organic acids in soil solutions (McRae and Monreal, 2011; Meyer et al., 2008; Uren, 2001).

The developments by Beckey (1977), Schulten (1987a,b, 1999), and Schulten et al., (1988) of soft ionization such as field ionization and field desorption (FD) mass spectrometry, following pyrolysis, have made it possible to identify major chemical structures in humic and fulvic acids, humins, and whole soils. Especially, pyrolysis-field ionization mass spectrometry (Py-FIMS) has been found useful to provide information at the molecular level on these complex organics. Recently, the chemical heterogeneity of organic molecules in water leachates of planted soil was characterized by Py-FIMS (Leinweber et al., 2008; Schlichting and Leinweber, 2009).

Taking advantage of our previous experiences with Py-FIMS, we applied this method to the identification of the major organic components of four soil solutions, collected at four different stages of wheat (*Triticum aestivum*) growth. As very little information on the organic components of the soil solution is available in the literature, and in view of its importance for nutrient cycling processes, plant and microbial growth, and interactions between root exudates and soil organisms, we believe that increasing our knowledge in this area is of fundamental importance for future developments in agriculture and the biological sciences.

For the first time, Py-FIMS has been used to comprehensively characterize the chemical composition of organic compounds in soil solutions obtained from the rhizospheres of wheat at four different phenological stages

of wheat growth. This chapter presents the organic components identified in soil solutions in classes of related chemical structures and linked to their biological sources and biochemical functions. We point at new ways of integrating chemistry, with microbiology and biochemistry in soil–plant systems for increasing our understanding of important and complex processes taking place in rhizospheres. We emphasize soil organic chemistry and biochemistry since they are essential disciplines, mostly displaced, by studies on the ecology of soil carbon. Understanding the interactions between these two scientific disciplines is essential to the unraveling of soil carbon dynamics and storage in soil systems. It is also our objective to stimulate interest in biological chemistry to better understand life processes in soil–plant systems.

2. MATERIALS AND METHODS

2.1. Soil samples

A bulk soil sample (1000 kg) was taken from the 0–20 cm depth of a fallowed field (uncropped for the past 15 years) located on the Central Experimental Farm of Agriculture and Agri-Food Canada in Ottawa, Ontario. The soil was a sandy loam with a pH of 6.6 in water and belongs to the Manotick series of the Haplorthods Great Soil Group. The bulk soil sample was passed through a 2-cm sieve to remove large stones and coarse plant fragments; it then was passed through a 1-mm-diameter sieve, mixed thoroughly, and stored for 2–3 days before transferring it to plastic pots. A porous fabric pocket (8 cm diameter × 15 cm height) containing 450 g of soil was placed at the center of each plastic pot and then 3.8 kg of soil was poured around the pocket in each pot (20 cm diameter × 15 cm height). The fabric pocket helped increase the root mass without limiting its spatial distribution within the pot, thus facilitating the collection of the soil solution and so simulating the crop rhizosphere. The ratio of plants per unit area of soil within the pots resembled the plant density used in field experiments (i.e., 4 plants/pot/314.16 cm^2 or 127 plants/m^2). A parallel series of unplanted soil pots containing the same amount of soil as the planted pots were incubated alongside.

2.2. Wheat growth

Six to eight seeds of wheat (*T. aestivum*, AC Barrie) were planted inside each fabric pocket. After emergence, only four plants per pot were grown to maturity. Wheat was grown under controlled conditions of light (350 μEinstein/m^2/s) and temperature (22 °C). Soil pots were kept moist

at 80% field capacity and did not receive any fertilizer during the growing season of wheat. A parallel series of pots containing only soil (unplanted soil pots) were incubated at the same temperature and soil moisture content (80% water holding capacity).

2.3. Collection of soil solutions

Planted and unplanted soil pots (four replicates each) were destructively sampled weekly to obtain soil solutions from the wheat rhizosphere and the unplanted soil pots. Roots and soil samples collected from the rhizosphere and from unplanted pots were handled and separated using gloves to prevent contamination by direct contact of the soil with hands. Soil solutions were obtained after placing 50 g of moist soil into a Vivacell 70 (Sartorius Stedim Biotech, USA), which was subsequently centrifuged at $2000 \times g$ for 10 min at 4 °C. Each collected solution sample was placed into a 10-mL glass vial and kept frozen at −18 °C until chemical analysis by mass spectrometry and a Shimadzu soluble carbon analyzer. Prior to use, the Vivacell 70 was conditioned as recommended by the manufacturer.

2.4. Four different growth stages of wheat

Soil solutions from four different growth stages were selected for investigation in this research study. These stages were (1) four leaves unfolded (referred to as IF031 occurred 25 days after seeding); (2) flag leaf, two tillers (IF093, 53 days after seeding); (3) seed—early milk stage (IF137, 72 days after seeding); and (4) seed—hard grain (IF196, 102 days after seeding).

2.5. Pyrolysis-field ionization mass spectrometry

Prior to Py-FIMS analysis, the volumes of the soil solution samples were reduced by evaporation from 1 mL to about 100 μL. Five microliter aliquots of each soil solution sample, in triplicate, were then transferred into quartz crucibles, which were freeze-dried and stored in a desiccator until mass spectrometric analyses. For Py-FIMS analysis, freeze-dried solutions in crucibles were placed into a quartz micro-oven and introduced into the vacuum chamber of a double-focusing Finnigan MAT 900 mass spectrometer (Finnigan, MAT, Bremen, Germany). When the pressure had dropped below 1.5×10^{-2} Pa, the quartz micro-oven with the freeze-dried sample was inserted into the ion source and heated under high vacuum (10^{-6} Pa) from 50 to 500 °C at a rate of 10 °C/min. During about 16 min of heating time, 46 magnetic scans were recorded over the mass range m/z 15–900 Da

(single spectra). The latter were combined to obtain a thermogram of total ion intensity (TII) of volatilized organic matter, and an averaged Py-FI mass spectrum. The Py-FIMS data were normalized to 1 μL solution sample, and the ion intensity (II) for each identified signal was computed. The sum of all IIs yielded the TIIs. The individual compounds identified were grouped into 11 compound classes. The II generated for each compound class was then expressed as the percentage of the TII. The II of each compound class was considered a semi-quantitative estimate of its concentration. For more details on the Py-FIMS method, the reader is referred to the following publications: Beckey (1977), Schulten (1987a,b), Schnitzer and Schulten (1992), Schnitzer and Schulten (1995), Schnitzer (2000), and Schnitzer and Monreal (2011).

2.6. Semi-quantitative estimations

The II for each m/z value was measured and then all II values for each class of compounds were added to obtain TII, a semi-quantitative estimate of its concentration.

2.7. Analysis of sugars and polysaccharides

The method which we used for carbohydrate analysis was proposed by Schulten (1984) and Kögel et al., (1988) and it is based on the assignment of mass signals due to sugars and polysaccharides in Py-FIMS spectra of soil and plant samples. The following mass signals were used for hexoses = m/z 126, 144, 162; pentoses = m/z 114, 132; and polysaccharides = m/z 60, 72, 82, 84, 96, 98, 110, 112. Hexoses include glucose, galactose, and mannose, while pentoses refer to arabinose and xylose.

2.8. Analysis of amino acids

For the analysis of amino acids by Py-FIMS, we used the following mass signals (Sorge et al., 1993): acidic amino acids = m/z 70, 84, 97, 99, 115; neutral amino acids = m/z 57, 73, 75, 87; neutral aromatic amino acids = m/z 74, 91, 120; and basic amino acids = m/z 60, 129, 135. Acidic amino acids include aspartic and glutamic acids. Neutral amino acids refer to glycine, alanine, leucine, isoleucine, valine, proline, hydroxyproline, serine, and threonine. Neutral aromatic amino acids include phenylalanine, tyrosine, and tryptophan, while basic amino acids are arginine, lysine, ornithine, and histidine.

2.9. Identification of remaining *m/z* signals

The assignments of the remaining *m/z* signals corresponding to phenols + lignin monomers, lignin dimers, alkylbenzenes, flavonoids, alkyl radicals, fatty acids + alkanes, nitrogen-containing compounds, steroids and sterols, and esters of suberin were in accordance with the identified compounds published earlier for soil humic substances (HSs) (Hempfling and Schulten, 1990; Schnitzer, 2000; Schnitzer and Monreal, 2011; Schnitzer and Schulten, 1995). For assignments of *m/z* signals for other organic compounds such as flavonoids, we used information from published work by Fabre et al. (2001) and the NIST Chemistry Webbook (http://webbook.nist.gov) of the National Institute of Standards and Technology of the USA.

3. THERMAL ANALYSIS OF THE SOIL SOLUTIONS BY Py-FIMS

The Py-FIMS spectra of the four soil solutions collected at four different growth stages of wheat are shown in Figs. 4.1–4.4. These spectra extend from *m/z* 15 to *m/z* 500–550. Figure 4.5 represents an expanded *m/z* axis in increments of 100 *m/z* units showing greater signal separation and details for Fig. 4.1. Figures 4.2–4.4 were also expanded to allow detailed analysis of Py-FIMS spectra but are not shown herein. Each spectrum in Figs. 4.1–4.4 shows in its top right side a plot of II versus temperature (thermogram). These are essentially differential thermal analysis (DTA) curves which show what happens to chemical components in soil solutions during pyrolysis. The purpose of pyrolysis is to volatilize the organic components in the soil solutions and to transfer them under high vacuum to the mass spectrometer in which they are ionized and separated in an electromagnetic field according to their molecular weights or *m/z* values, where m = mass and z = charge. The *m/z* values can then be used for identifying the organic compounds. Note in Fig. 4.1 the small exothermic maximum at 350 °C, which indicates that organic compounds, which can be volatilized at this temperature, do so. The maximum volatilization temperatures in Figs. 4.2 and 4.3 are similar to that in Fig. 4.1. Schlichting and Leinweber (2009) showed that carbohydrates, and phenols + lignin monomers from soil water leachates were volatized by pyrolysis at 375 °C. In Fig. 4.4, the volatilization maximum temperature increased to 390 °C with an additional shoulder at 440 °C, which indicated the volatilization of the remaining organic components with higher molecular weight, and structurally more complex, and therefore more difficult to volatilize than the organics in the first three soil

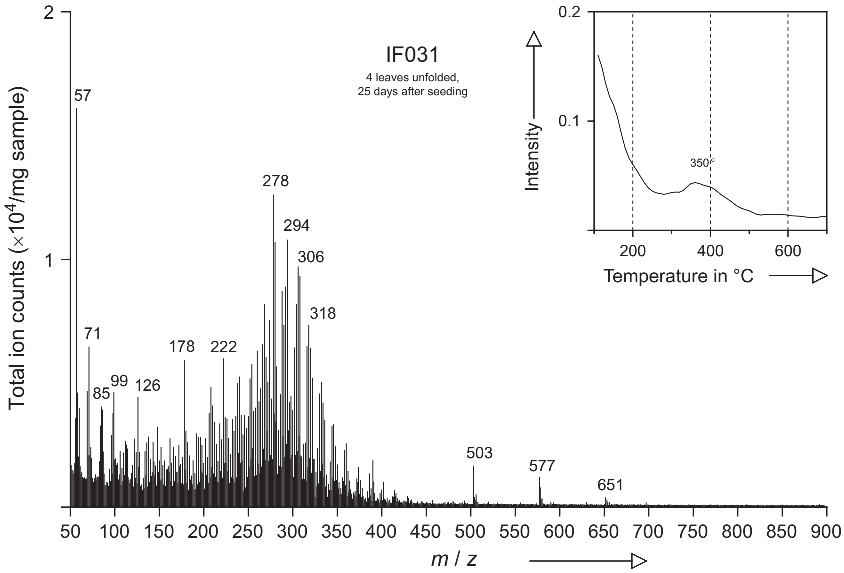


Figure 4.1 Py-FIMS spectrum of soil solution IF031 (four leaves unfolded, 25 days after wheat seeding).

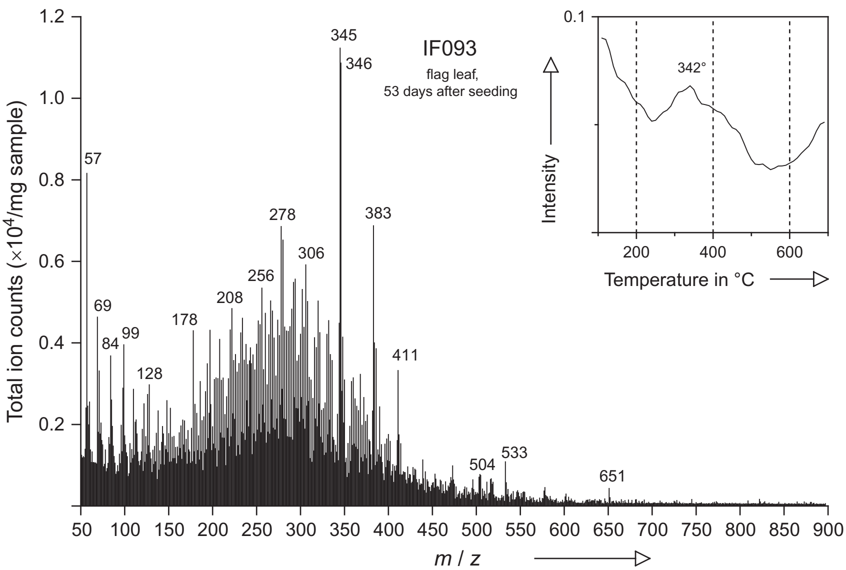


Figure 4.2 Py-FIMS spectrum of soil solution IF093 (flag leaf, 53 days after wheat seeding).

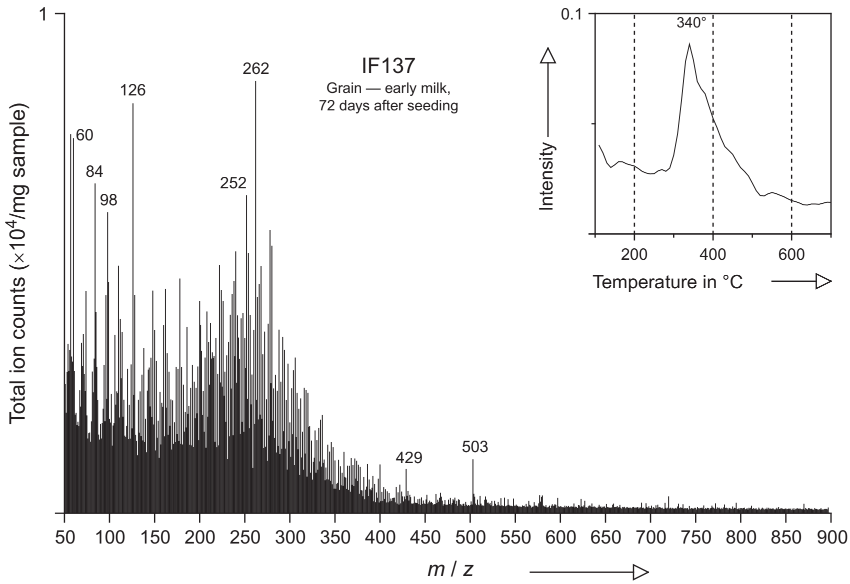


Figure 4.3 Py-FIMS spectrum of soil solution IF137 (grain—early milk, 72 days after wheat seeding).

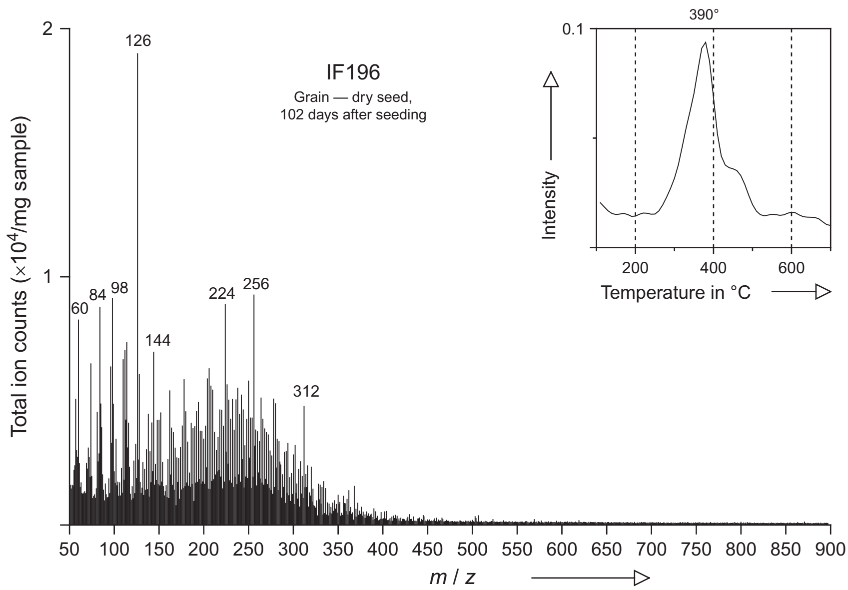


Figure 4.4 Py-FIMS spectrum of soil solution IF196 (grain—dry seed, 102 days after wheat seeding).

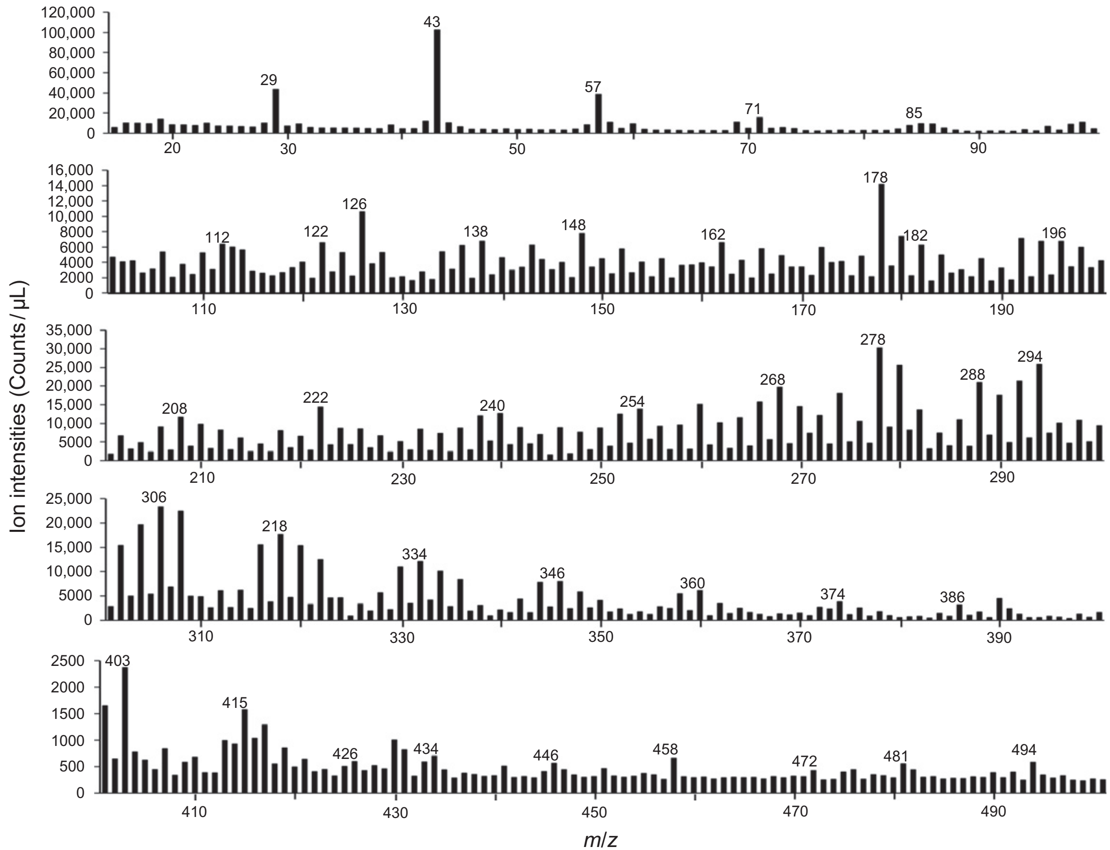


Figure 4.5 Expanded *m/z* axis of Py-FIMS spectrum of soil solution presented in Fig. 4.1 to show greater signal separation and detail.

solution samples. The DTA curves in Figs. 4.1–4.4 show that the pyrolysis of the soil solution samples is completed under 500–550 °C. Lipids extracted by water leaching from potato planted soil samples have a maximum volatilization peak at 450–525 °C (Schlichting and Leinweber, 2009). It is also noteworthy that the DTA curve of a fulvic acid extracted from the Bh horizon of a Spodosol (Schnitzer and Khan, 1972) is very similar to that shown in Fig. 4.4, with approximately the same volatilization maximum temperature of 450 °C.

4. MASS SPECTROMETRIC ANALYSIS OF THE FOUR SOIL SOLUTIONS AT THE FOUR STAGES OF WHEAT GROWTH

4.1. Analysis of the chemical components in soil solutions by Py-FIMS

The data in Table 4.1 show *m/z* values and their corresponding IIs at the four growth stages of wheat. The mass spectra in Figs. 4.1–4.4 show that the soil solution may contain at least 500 different chemical components over the range of *m/z* 15–500. Of these, we have identified 346 components (about 70% of total) by Py-FIMS. In order to simplify this complex system, we grouped the identified components into the following 11 chemical classes: carbohydrates, amino acids, phenols + lignin monomers, lignin dimers, *n*-alkylbenzenes, flavonoids, alkyl radicals, saturated + unsaturated fatty acids + *n*-alkanes, N-compounds, sterols + steroids, and esters of suberin. We have listed in Tables 4.1–4.13 the identity of each component in terms of *m/z* (i.e., molecular weight) and II (as semi-quantitative estimate of concentration) for each component class at the four stages of wheat growth. The results are summarized in Table 4.14, which shows the percentage of each class relative to the TII of all chemical classes. Table 4.14 also depicts the effects of the four different wheat growth stages on the concentrations of the identified chemical classes.

4.2. Carbohydrates in the soil solutions

4.2.1 Py-FIMS analysis of carbohydrates

The data in Table 4.1 show *m/z* values for hexoses, pentoses, and polysaccharides in soil solutions and how their concentrations vary at the four different growth stages of wheat. As indicated by the subtotals, the concentrations of hexoses, pentoses, and polysaccharides in the soil solution increased continuously throughout the growing season of wheat from the four leaf (25 days after seeding) to the flag leaf (53 days after seeding) and

Table 4.1 Ion intensities (IIs) for *m/z* assigned to carbohydrates in soil solutions obtained from the rhizosphere at four different growth stages of wheat

	II (count × 10^2/μL) at wheat growth stage			
m/z	**IF031**[a]	**IF093**[b]	**IF137**[c]	**IF196**[d]
	Hexoses			
126	106.23	86.51	159.05	318.29
144	43.75	55.89	56.42	116.73
162	66.09	56.75	87.03	90.58
Subtotal	216.07	199.15	302.50	525.60
	Pentoses			
114	56.29	55.94	70.16	123.36
132	27.88	43.28	43.87	42.13
Subtotal	84.17	99.22	114.03	165.49
	Polysaccharides			
60	95.63	80.70	145.55	138.41
72	49.65	55.83	53.83	45.51
82	28.96	53.09	46.79	42.67
84	78.58	116.42	127.93	146.78
96	69.24	62.63	84.51	106.77
98	90.48	91.45	116.72	152.87
110	52.46	90.57	96.01	111.62
112	63.90	64.97	75.28	117.91
Subtotal	528.90	615.66	746.62	862.54
Total	829.14	914.03	1163.15	1553.63

[a]IF031 = four leaves unfolded (25 days after seeding).
[b]IF093 = flag leaf (53 days after seeding).
[c]IF137 = grain—early milk (72 days after seeding).
[d]IF196 = grain—dry seed (102 days after seeding).

early milk-grain (72 days after seeding), to the seed hard grain stage (102 days after seeding). The most abundant *m/z* signals for carbohydrate components in the soil solutions were polysaccharides > hexoses > pentoses. Leinweber et al. (2008) reported that *m/z* values of sugars, together with those of amino acids and polyamines, had the strongest discriminating powers of all the

organic compounds found in soil water leachates during the first 21 days of maize growth.

4.2.2 Biochemistry and functions of carbohydrates in soil–plant systems

Living cells of plants, soil heterotrophs, and insects use sugars (i.e., mono- and polysaccharides) mainly as a source of energy and as precursors for the synthesis of many of their structural and metabolic components (Finch et al., 1971). Carbohydrates are the backbones for cellulose and hemicellulose plant structures. In plants, sugars are synthesized to form the backbones for heteropolymers and polysaccharides such as cellulose, hemicellulose, and starch and may be stored as sources of energy. Simple sugars and polysaccharides are also synthesized by soil bacteria and fungi and other soil organisms (Quastel, 1965). Once excreted from microbial cells, polysaccharides become involved in soil aggregation and improvement of soil structure (Geoghegan and Brian, 1946; Rillig and Mummey, 2006). At any point in time, the content and types of mono- and polysaccharides in soil solutions will depend on the interactions between abiotic and biotic components and processes catalyzed by plants, microorganisms, and extracellular enzymes influencing the decomposition of plant residues and soil organic matter or HSs, especially within rhizospheres. The relative quantitative contributions of plants and microorganisms to the carbohydrate content of soil solutions during the growing season of crops remain unknown. As crops depend on soil inorganic nutrients, especially nitrogen, which is supplied by the mineralizing activities of soil microorganisms, exudation of carbohydrates by crops help satisfy the need of carbon and energy by soil heterotrophs and also create a favorable milieu for their growth.

4.3. Free amino acids in soil solutions

4.3.1 Py-FIMS analysis of free amino acids

Table 4.2 presents analytical data for amino acids and how their concentrations varied during the four growth stages of wheat. Total amino acids were subdivided into acidic, neutral, neutral aromatic, and basic amino acids. Table 4.2 shows that with an increase in the number of growing days of wheat, we observed relatively small increases in the concentrations of acidic and neutral aromatic amino acids and decreases in the concentrations of neutral and basic amino acids. Note that the maximum concentrations of acidic and basic amino acids in soil solutions were observed at the flag leaf stage, 53 days after seeding. The highest concentration of amino acids was shown

Table 4.2 Ion intensities (II) for *m/z* assigned to amino acids in soil solutions obtained from the rhizosphere at four different growth stages of wheat

	II (count × 10^2/μL) at wheat growth stage			
m/z	**IF031**[a]	**IF093**[b]	**IF137**[c]	**IF196**[d]
	Acidic amino acids			
70	49.73	57.25	56.99	37.85
84	78.58	116.42	127.93	146.78
97	31.98	42.17	44.29	55.25
99	110.77	125.13	89.64	81.69
115	28.68	41.77	37.36	52.04
Subtotal	299.74	382.74	356.21	373.61
	Neutral amino acids			
57	386.66	258.07	147.13	84.86
73	57.49	64.42	47.22	32.23
75	27.59	47.44	37.84	32.85
87	53.44	46.52	43.76	33.92
Subtotal	525.18	416.45	275.95	183.86
	Neutral aromatic amino acids			
74	47.38	50.83	86.19	108.85
91	23.84	26.51	28.88	20.53
120	40.25	59.50	55.92	25.89
135	30.88	34.33	29.73	23.44
Subtotal	142.35	171.17	200.72	178.71
	Basic amino acids			
129	20.12	41.25	30.27	28.74
135	30.88	34.33	29.73	23.44
60	95.63	80.70	145.55	138.41
Subtotal	51.00	75.58	60.00	52.18
Total	1018.27	1045.94	892.88	788.36

[a]IF031 = four leaves unfolded (25 days after seeding).
[b]IF093 = flag leaf (53 days after seeding).
[c]IF137 = grain—early milk (72 days after seeding).
[d]IF196 = grain—dry seed (102 days after seeding).

by *m/z* 99, a biomarker for an acidic amino acid; *m/z* 57, a neutral amino acid; *m/z* 74, a neutral aromatic amino acid; and *m/z* 60, a basic amino acid.

4.3.2 Biochemistry and function of amino acids in soil–plant systems

Amino acids are synthesized by plants and soil organisms and found free in soil solutions (Henry and Jefferies, 2002; Monreal and McGill, 1989a). Amino acids are used for energy production and the biosynthesis of structural proteins, enzymes, and alkaloids in plants and other living organisms (Lehninger, 1982). Short peptides of D-amino acids are essential components of bacterial peptidoglycan in cell walls, and some D-amino acids exist in soil organic matter at 10–20% of the concentration of L-enantiomers (Amelung, 2003; Amelung et al., 2006). Evidence also shows that *Arabidopsis thaliana* metabolizes D-amino acids, and D-amino acid racemases (Gördes et al., 2011).

The content of free amino acids in soil solutions is low due to their high turnover rates associated with microbial utilization (Anraku, 1980; Monreal and McGill, 1989a,b). Although most N enter soil ecosystems as proteins and heterocyclic N, free amino acids in soil solutions are substrates for the microbial production and rapid supply of mineral-N to plants via deamination to ammonia and its subsequent nitrification in warm and cool climate soils. Hill et al. (2011a) showed that sterilized wheat roots also assimilate peptides and free amino acid N at rates comparable to those of inorganic N forms. In other terrestrial ecosystems with limited N supply at high latitudes, the supply of nitrogen also regulates primary productivity (Liu and Greaver, 2010). Depending on their growing environment, some plant species prefer the uptake of peptides and amino acids to mineral-N residing in soil solutions, especially in Antarctic soils where rates of organic N mineralization are low (Hill et al., 2011b). The amino acid composition of soil solutions together with inorganic colloids and the reactions between biotic and abiotic pools help control the production of plant biomass and the flow directions of C and N in nutrient cycling, and energy between biotic and abiotic soil components (Monreal and McGill, 1989b). The presence of amino acids in root exudates, and thus soil solutions, helps inhibit the population of nematodes and the growth of competitive plant species (Bertin et al., 2003) or stimulate the preferential growth of bacteria in rhizospheres (Guirguis et al., 1969). Amino acids are precursors for several important and complex molecules of biological importance such as heterocyclic-N compounds and polyketides (PKTs) (Siebenberg et al., 2011).

4.4. Phenols, lignin monomers, and lignin dimers in soil solutions

4.4.1 Py-FIMS analysis of phenols, lignin monomers, and lignin dimers

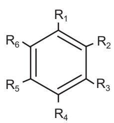
The chemical structures of the phenols and lignin monomers identified are presented in Table 4.3, while effects of the four wheat growth stages on the concentrations of these compounds are shown in Table 4.4. The most prominent phenol was trihydroxybenzene followed by dihydroxybenzene. The abundance of these two compounds in soil solutions collected at the hard grain stage doubled and tripled, respectively, relative to their concentration observed at the early stage of wheat growth. Coniferyl aldehyde, followed by syringyl aldehyde, was the most abundant lignin monomer in soil solutions. Overall, Table 4.4 shows that the concentrations of phenols and lignin monomers in soil solution at the grain—dry seed stage were about 15% higher than those at the first four-leaf unfolded stage of wheat growth.

As shown in Table 4.5, two types of lignin dimers were identified in the soil solutions: those with biphenyl and those with phenylcoumaran structures. Both types of lignin dimers reached maximal concentrations at the flag leaf stage, 53 days after seeding. Thereafter, the abundance of IIs for both types of structures decreased by almost two-thirds when wheat reached its grain-forming stage. In addition, the concentrations of total biphenyls were consistently lower than those of phenylcoumarans. The most prominent biphenyl was m/z 274, followed by m/z 260, 302, and 316 with similar concentration. The most abundant phenylcoumarans were m/z 332 and 330, especially during the first two wheat growth stages. The least abundant lignin dimer was m/z 356 (Table 4.6).

4.4.2 Biochemistry and functions of phenols, lignin monomers, and dimers in soil–plant systems

Phenols and lignin monomers are precursors of phenylpropanoid macromolecules when lignin is synthesized during plant growth (Hatfield and Vermerris, 2001). Lignin strengthens the secondary cell walls and phenols, and among other functions, it regulates the elongation of plant cells. Phenols and lignin monomers are also produced by fungi and exuded by plant roots into soils (Martin et al., 1967; Packter and Steward, 1967). In addition, monomeric, dimeric, and polymeric phenolics form the backbone structure of secondary metabolites such as flavonoids, biflavonoids, and isoflavonoids (Lattanzio et al., 2006). Simple phenolic acids such as *trans*-cinnamic and *p*-coumaric acids are precursors for the biosynthesis of more complex compounds including flavonoids, tannins, lignins, and anthocyanins (Winkel-Shirley, 2002). Plants

Table 4.3 Chemical structures for *m/z* assigned to phenols and lignin monomers in soil solutions obtained from the rhizosphere at four different growth stages of wheat

m/z	Structure	R_1	R_2	R_3	R_4	R_5	R_6
94		—OH	—H	—H	—H	—H	—H
108		—OH	$—CH_3$	—H	—H	—H	—H
110		—OH	—OH	—H	—H	—H	—H
122		—OH	$—CH_3$	$—CH_3$	—H	—H	—H
124		—H	—H	$—OCH_3$	—OH	—H	—H
126		—H	—H	—OH	—OH	—OH	—H
138		$—CH_3$	—H	$—OCH_3$	—OH	—H	—H
140		—OH	—H	$—OCH_3$	—OH	—H	—H
150		$—CH{=}CH_2$	—H	$—OCH_3$	—OH	—H	—H
152		—CHO	—H	$—OCH_3$	—OH	—H	—H
154		—H	—H	$—OCH_3$	—OH	$—OCH_3$	—H
164		$—CH_2—CH{=}CH_2$	—H	$—OCH_3$	—OH	—H	—H
166		$—CH_2—CH_2—CH_3$	—H	$—OCH_3$	—OH	—H	—H
168		—COOH	—H	$—OCH_3$	—OH	—H	—H
178		—CH=CH=CHO	—H	$—OCH_3$	—OH	—H	—H
180		$—CH{=}CH—CH_2OH$	—H	$—OCH_3$	—OH	—H	—H

Continued

Table 4.3 Chemical structures for *m/z* assigned to phenols and lignin monomers in soil solutions obtained from the rhizosphere at four different growth stages of wheat—cont'd

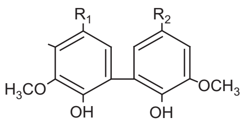
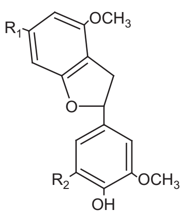
m/z	Structure	R_1	R_2	R_3	R_4	R_5	R_6
182		—CHO	—H	$—OCH_3$	—OH	$—OCH_3$	—H
194		—CH═CH═COOH	—H	$—OCH_3$	—OH	$—OCH_3$	—H
196		$—CH_2—CHO$	—H	$—OCH_3$	—OH	$—OCH_3$	—H
208		—CH═CH—CHO	—H	$—OCH_3$	—OH	$—OCH_3$	—H
210		$—CH═CH—CH_2OH$	—H	$—OCH_3$	—OH	$—OCH_3$	—H
212		$—CH_2—COOH$	—H	$—OCH_3$	—OH	$—OCH_3$	—H

Table 4.4 Ion intensities (II) for *m/z* assigned to phenols and lignin monomers in soil solutions obtained from the rhizosphere at four different growth stages of wheat

		II (count × 10^2/μL) at wheat growth stage			
m/z	**Identity**	**IF031**[a]	**IF093**[b]	**IF137**[c]	**IF196**[d]
		Phenols			
94	Phenol	36.45	40.22	57.38	31.19
108	Methylphenol	37.20	43.79	47.17	38.17
110	Dihydroxybenzene	52.46	90.57	96.01	111.62
122	Dimethylphenol	66.00	79.29	41.93	43.21
124	Guaiacol	52.89	53.80	57.63	54.48
126	Trihydroxybenzene	106.23	86.51	159.05	318.29
138	Methylguaiacol	67.90	73.76	63.91	74.78
140	Hydroxyguaiacol	46.11	42.83	36.55	49.56
150	Ethyleneguaiacol	44.69	56.19	70.91	70.71
152	Vanillin	57.62	75.78	58.98	75.74
154	Syringol	40.30	53.36	35.79	42.24
		Lignin monomers			
164	Guaiacylpropene	42.60	62.07	61.97	65.50
166	Guaiacylpropane	57.92	66.64	54.82	62.41
168	Vanillic acid	48.87	66.06	44.04	51.91
178	Coniferyl aldehyde	141.92	135.99	90.98	98.14
180	Coniferyl alcohol	73.57	78.86	56.58	76.47
182	Syringyl aldehyde	62.80	71.90	49.77	55.98
194	Ferulic acid	67.72	110.36	50.93	82.81
196	Syringyl acetaldehyde	67.74	71.95	48.53	63.32
208	Sinapyl aldehyde	116.08	129.29	78.22	93.80
210	Sinapyl alcohol	97.93	97.53	66.30	91.09
212	Syringyl acetic acid	82.36	99.24	73.68	62.56
Subtotal phenols		298.34	340.38	401.54	542.48
Subtotal lignin monomers		1095.45	1266.75	943.01	1095.03
Total		1393.79	1607.13	1344.55	1637.51

[a]IF031 = four leaves unfolded (25 days after seeding).
[b]IF093 = flag leaf (53 days after seeding).
[c]IF137 = grain—early milk (72 days after seeding).
[d]IF196 = grain—dry seed (102 days after seeding).

Table 4.5 Chemical structures for *m/z* assigned to lignin dimers in soil solutions obtained from the rhizosphere at four different growth stages of wheat

m/z	Structure	R$_1$	R$_2$
246	Biphenyl	—H	—H
260		—CH$_3$	—H
272		—CH$_3$	—CH$_3$
274		—CH$_2$CH$_3$	—H
286		—CH=CH—CH$_3$	—H
300		—CH=CH—CH$_3$	—CH$_3$
302		—CH=CH—CH$_2$—OH	—H
316		—CH=CH—CH$_2$—OH	—CH$_3$
328		—CH=CH—CH$_2$—OH	—CH=CH$_2$
314	Phenylcoumaran	—CH—CH—OH	—H
330		—CH$_2$—OH	—OCH$_3$
332		—CH$_2$—0H	—OCH$_3$
340		—CH=CH—CH$_3$	—OCH$_3$
342		—CH=CH—CH$_3$	—OCH$_3$
346		—CH$_2$—CH$_2$—OH	—OCH$_3$
356		—CH=CH—CH$_2$—OH	—OCH$_3$
358		—CH=CH—CH$_2$—OH	—OCH$_3$

need phenolic compounds for pigmentation, growth, reproduction, resistance to pathogens, and many other functions. Phenols and lignin-based structures can also occur in soil solutions due to the decomposition of plant residues and nonliving soil organic matter. When excreted from plant roots, phenols can exert inhibitory growth function within rhizospheres potentially affecting biotic and abiotic components in soil–plant relations (Kefeli et al., 2003). Phenolic compounds are the main class of secondary metabolites in plants, and many such compounds have been identified in various plant species (Horbowicz et al., 2011). Phenolic compounds are important for plants due to their various biological functions including UV protection, pollen tube growth, antimicrobial activity, and insect resistance (Stein et al., 2002; Winkel-Shirley, 2002). In soil systems, phenols, lignin monomers, and lignin

Table 4.6 Ion intensities (II) for *m/z* assigned to lignin dimers in soil solutions obtained from the rhizosphere at four different growth stages of wheat

	II (count × 10^2/μL) at wheat growth stage			
m/z	**IF031**[a]	**IF093**[b]	**IF137**[c]	**IF196**[d]
	Biphenyls			
246	88.74	117.23	75.52	53.50
260	151.16	149.49	71.05	62.99
272	120.75	100.80	70.38	60.87
274	181.04	144.21	44.09	49.96
286	108.95	135.47	47.41	40.61
300	93.99	133.28	35.09	47.35
302	154.30	167.99	48.34	53.68
316	155.83	130.55	48.56	39.97
328	56.71	79.98	32.01	27.55
Subtotal	1111.47	1159.00	472.45	436.48
	Phenylcoumarans			
314	62.04	83.51	31.51	34.13
330	109.64	133.17	28.19	26.89
332	120.94	143.88	32.92	25.34
340	21.75	47.10	17.56	14.21
342	43.69	71.14	26.45	11.90
346	80.12	343.67	27.45	16.38
356	28.36	61.86	18.07	19.41
358	54.70	96.57	15.51	14.31
Subtotal	281.37	980.90	106.39	85.68
Total	1632.71	2139.90	670.11	599.05

[a]IF031 = four leaves unfolded (25 days after seeding).
[b]IF093 = flag leaf (53 days after seeding).
[c]IF137 = grain—early milk (72 days after seeding).
[d]IF196 = grain—dry seed (102 days after seeding).

dimers have been thought to be precursors of HSs (Flaig, 1988). A chemical pathway of HS formation from phenols or lignin components has not been demonstrated thus far.

4.5. Alkylbenzenes in soil solutions

4.5.1 Py-FIMS analysis of alkylbenzenes

The data in Table 4.7 show the Py-FIMS analysis of *n*-alkylbenzenes in the soil solutions obtained at the four different growth stages of wheat. The *n*-alkylbenzenes identified ranged from *n*-methyl to *n*-uncosylbenzenes. The II data show that the maximum concentration of *n*-alkylbenzenes was reached at the flag leaf stage but decreased by one-third when the wheat reached its grain-forming stage. The latter concentration was similar to

Table 4.7 Ion intensities (II) for *m/z* assigned to *n*-alkylbenzenes in soil solutions obtained from the rhizosphere at four different growth stages of wheat

		II (counts × $10^2/\mu L^1$) at wheat growth stage			
m/z	**Identity**	**IF031**[a]	**IF093**[b]	**IF137**[c]	**IF196**[d]
92	Methylbenzene	23.38	31.32	34.83	18.25
106	Ethylbenzene	53.60	48.38	69.11	28.49
120	Propylbenzene	40.25	59.50	55.92	25.89
134	Butylbenzene	53.87	46.20	47.14	37.55
148	Pentylbenzene	77.47	81.76	86.30	70.65
162	Hexylbenzene	66.09	56.75	87.03	90.58
176	Heptylbenzene	48.10	60.30	55.88	66.83
190	Octylbenzene	32.54	69.15	48.92	66.41
204	Nonylbenzene	48.13	99.33	47.23	98.69
218	Decylbenzene	80.67	98.71	67.88	77.69
232	Undecylbenzene	84.68	134.36	66.35	84.77
344	Nonadecylbenzene	78.48	141.86	23.77	14.82
372	Uncosylbenzene	27.28	84.19	21.08	14.72
Total		714.54	1011.81	711.04	695.34

[a]IF031 = four leaves unfolded (25 days after seeding).
[b]IF093 = flag leaf (53 days after seeding).
[c]IF137 = grain—early milk (72 days after seeding).
[d]IF196 = grain—dry seed (102 days after seeding).

that observed at the early four-leaf growth stage. The most abundant *n*-alkylbenzenes were decyl-, undecyl-, and nondecylbenzene at the flag leaf stage, 53 days after seeding.

4.5.2 Biochemistry and functions of alkylbenzenes in soil–plant systems

Earlier, Schnitzer and Monreal (2011) used the term alkylbenzenes interchangeably with the term polyketide alkylaromatics to denote a specific group of natural products synthesized by plants, animals, and soil microorganisms (Hertweck, 2009). Living organisms synthesize alkylaromatic structures abundantly, and they may undergo decomposition once excreted into their surroundings. Alkylbenzenes in soil solutions may also be a result of the depolymerization and decomposition reactions of plant tissues. Aromatic–aliphatic PKTs provide ecological protection and advantages to soil microorganisms and plants during periods of environmental and abiotic stress (Das and Khosla, 2009). From a functional viewpoint, PKTs include a large class of diverse compounds, including antibiotics, pigments, and regulatory substances associated with sporulation and cell differentiation processes. Their bioactivity may depend on the particular chemical structure and not just on their amount (Firn and Jones, 2003). For example, *Bacillus subtilis*, a soil bacteria, synthesizes a variety of alkylaromatic PKTs through complex gene–enzyme systems from simple oxoacids via long-chain fatty acyl-coenzyme A (CoA) thioesters and malonyl-CoA, to yield various types of alkylpyrone methyl ethers such as triketide pyrones (Austin and Noel, 2003; Nakano et al., 2009). Alkylaromatic PKTs such as phenolic lipids appear to localize in cell membranes and play a role in modulating the rigidity and properties of the membrane, as during encystment by fungi (Funa et al., 2006). Schnitzer and Monreal (2011) proposed that a large diversity of microbially synthesized alkylaromatics serves as central structural units of soil organic matter during the synthesis of HS.

4.6. Flavonoids in the soil solution

4.6.1 Py-FIMS analysis of flavonoids

The chemical structures of seven flavonoids identified are listed in Table 4.8. Three of these structures were flavones, two were flavonones, and two were flavonols. In our study, the contents of the three flavones and the two flavonones were similar but higher than those of the two flavonols at all four stages of wheat growth. The IIs of flavones and flavonols reached their maxima at the flag leaf stage, 53 days after seeding, while the maxima for the flavonones were observed at the early four-leaf stage, 25 days after seeding. The abundance of the two flavonones decreased steadily from the four-leaf

Table 4.8 Ion intensities (II) and chemical structures of *m/z* assigned to flavonoids in soil solutions obtained from the rhizosphere at four different growth stages of wheat

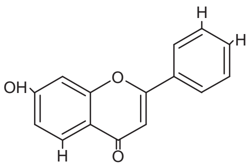
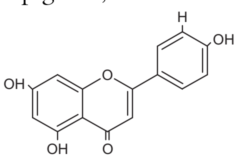
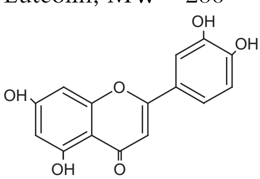
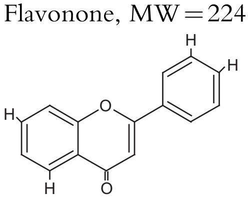
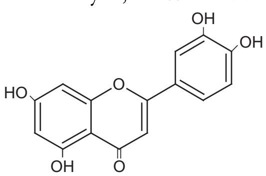
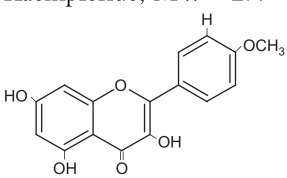
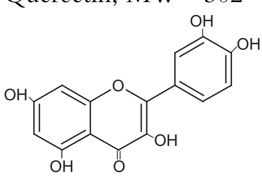
	II (count × 10^2/μL) at wheat growth stage			
Structure	**IF031[a]**	**IF093[b]**	**IF137[c]**	**IF196[d]**
Flavones				
Flavone, MW[e] = 222	143.63	153.16	96.27	66.69
	Also called tricin (found in wheat leaves and grain)			
Apigenin, MW = 270	144.89	130.36	61.55	62.36
	(Found in wheat)			
Luteolin, MW = 286	74.12	135.47	53.61	56.34
	(Found in wheat)			
Flavonones				
Flavonone, MW = 224	87.08	112.86	86.58	148.85
	(Found in wheat)			

Table 4.8 Ion intensities (II) and chemical structures of *m/z* assigned to flavonoids in soil solutions obtained from the rhizosphere at four different growth stages of wheat—cont'd

	II (count × 10^2/μL) at wheat growth stage			
Structure	**IF031**	**IF093**	**IF137**	**IF196**
Eriodictyol, MW = 288	50.37	65.12	27.81	20.63
	(Found in wheat and other cereals, root exudates)			
Flavonols				
Kaempferide, MW = 299	50.37	65.12	27.81	20.63
	(Found in cereals: wheat, barley)			
Quercetin, MW = 302	154.30	167.99	48.34	53.68
	(Found in wheat)			
Flavones	397.47	418.99	205.23	169.66
Flavonones	296.31	251.97	157.72	182.85
Flavonols	204.67	233.11	76.15	74.31
Total	898.45	904.07	439.10	426.82

[a]IF031 = four leaves unfolded (25 days after seeding).
[b]IF093 = flag leaf (53 days after seeding).
[c]IF137 = grain—early milk (72 days after seeding).
[d]IF196 = grain—dry seed (102 days after seeding).
[e]MW = molecular weight.

unfolded stage to the late grain-forming stage of wheat. Quercetin, followed by flavone and apigenin, was the most abundant flavonoid. With the exception of flavonones, the concentration of all other flavonoid structures in the soil solutions of the wheat rhizosphere was always the lowest at the hard grain stage. Future research is warranted on the ecological functions of flavonoids in soil solutions and their potential role in soil solution metabolomics and in the synthesis of soil HSs.

4.6.2 Biochemistry and functions of flavonoids in soil–plant systems

For the first time, this chapter reports the presence of flavonoids in soil solutions. The presence of flavonoids in the soil solution of our study occurs during the four stages of wheat growth and appears associated with root exudation. The assignment of m/z values to flavonoids was based on comparison between selected m/z values from the Py-FIMS analysis of soil solutions and information on m/z values reported by the National Institute of Standards and Technology of the USA. Also, our identification of flavonoids is well supported by published evidence for their wide presence in tissues and especially root exudates of many different plant species (Hassan and Mathesius, 2012; Steinkellner et al., 2007). All three subclasses of flavonoids reported in the previous subsection have been found in wheat, other cereals, and leguminous plants. For example, quercetin, which was the flavonoid with highest concentration in soil solutions, has been found in root exudates to confer resistance to Al and Si in wheat (Kidd et al., 2001). Flavonoids are synthesized by many plant species and exuded from many plant roots, including cereal (Corcuera, 1984), cruciferae (Ponce et al., 2004), and leguminous plants (Aguilar et al., 1988). Flavonoids, however, are almost completely absent in bacteria, fungi, and algae (Lattanzio et al., 2006), but they can also be found in the seeds and fruits of many plant species (Grotewold, 2006). The flavonoid content of plant tissues and grains ranges from a few microgram to milligram per gram of material depending on the plant species (Adom and Liu, 2002; Crozier et al., 1997; Tolonen and Uusitalo, 2004). Flavonoids are phenylpropanoid secondary metabolites, most of which are synthesized from *p*-coumaroyl-CoA and malonyl-CoA and share the same precursors responsible for the synthesis of lignin in plants (Stafford, 1990). Flavonoids play important roles as signal molecules in plant–microbe interactions such as symbiosis (Bolaños-Vásquez and Werner, 1997; Steinkellner et al., 2007), antipathogenics (Bollina et al., 2010; Steinkellner et al., 2007), and establishment of vesicular arbuscular mycorrhizae in plant roots (Vivanco et al., 2002). The amounts of different

Table 4.9 Ion intensities (II) for *m/z* assigned to alkyl radicals in soil solutions obtained from the rhizosphere at four different growth stages of wheat

		II (count × 10^2/μL) at wheat growth stage			
m/z	**Identity**	**IF031[a]**	**IF093[b]**	**IF137[c]**	**IF196[d]**
15	Methyl	57.86	60.00	62.64	41.09
29	Ethyl	437.26	231.35	170.74	100.47
43	Propyl	1027.22	582.85	364.75	195.76
57	Butyl	386.66	258.07	147.13	84.86
71	Pentyl	155.15	104.80	69.38	52.02
85	Hexyl	96.94	82.30	77.94	81.74
99	Heptyl	110.77	125.13	89.64	81.69
113	Octyl	60.11	66.83	52.24	70.90
Total		2331.97	1511.33	1034.46	708.53

[a]IF031 = four leaves unfolded (25 days after seeding).
[b]IF093 = flag leaf (53 days after seeding).
[c]IF137 = grain—early milk (72 days after seeding).
[d]IF196 = grain—dry seed (102 days after seeding).

flavonoids exuded from root seedlings range from picomoles to nanomoles (Bolaños-Vásquez and Werner, 1997). Flavonoids may be also derived from the decomposition of plant remnants.

4.7. Py-FIMS analysis of alkyl radicals

The radicals identified in the four soil solutions (Table 4.9) ranged from methyl to octyl, that is, from C_1 to C_8, and were present in significant concentrations, especially the propyl radical. The highest concentrations of each alkyl radical were detected at the first phenological growth stage, four leaves unfolded. The total concentrations of alkyl radicals in the soil solutions decreased steadily by two-thirds from the early four-leaf stage, 25 days after seeding, to the dry grain stage, after 102 days of wheat growth. It is likely that these radicals were generated by chemical and/or enzymatic reactions from aliphatic side chains bonded to long aliphatic chains, especially near double bonds, in fatty acids, alkanes, and alkenes. It is also possible that free radicals were formed during pyrolysis or in the electromagnetic field of the mass spectrometer. Further research is needed to understand the formation and potential functions of free radicals in soil solutions.

4.8. Saturated and unsaturated fatty acids and alkanes in the soil solutions

4.8.1 Py-FIMS analysis of fatty acids and n-alkanes

The fatty acids listed in Table 4.10 include *n*-fatty acids, unsaturated fatty acids with one double bond, unsaturated fatty acids with two or more double bonds, and *n*-alkanes in soil solutions. The content of unsaturated fatty acids was almost three times higher than that of saturated fatty acids, and the content of unsaturated fatty acids with $\geq$2 double bonds was twice as large as that of unsaturated fatty acids with 1 double bond. By Py-FIMS, it is not possible to distinguish between fatty acids with one double bond and *n*-alkanes. Evidence from related research shows that *n*-alkanes are present in soil organic matter (Schnitzer and Schulten, 1995). In this study, we assumed that 50% of the II assigned to fatty acids with one double bond was due to unsaturated fatty acids with one double bond and 50% to *n*-alkanes. As presented in Table 4.10, *n*-fatty acids identified in the soil solutions ranged from n-C_1 to n-C_{38}, unsaturated fatty acids with one double bond from $C_{4:1}$ to $C_{38:1}$, unsaturated fatty acids with two double bonds from $C_{11:2}$ to $C_{22:2}$, and those with three double bonds per molecule extended from $C_{18:3}$ to $C_{22:3}$. Normal alkanes in soil solutions ranged from n-C_4 to n-C_{40}. Unsaturated fatty acids with one and $\geq$2 double bonds, especially those with more than 10 C atoms in length, were always more abundant than their saturated fatty acid counterparts at all sampling dates. Unsaturated fatty acids with $\geq$2 double were always more abundant than unsaturated fatty acid with one double bond. The most abundant saturated fatty acids were n-$C_{16} > n$-$C_{17} > n$-$C_{15} > n$-$C_{18} > n$-C_{19} ($>10^5$ counts/μL) >> other saturated fatty acids. In general, the content of fatty acids $>n$-C_{25} was very low ($<$1000 counts/μL). The most abundant unsaturated fatty acids with one, two, or more double bonds ranged from C_{15} to C_{22} in chain length (100,000–300,000 counts/μL); whereas, the most abundant *n*-alkanes ranged from n-C_{17} to n-C_{21} (12,000–190,000 counts/μL).

Based on data shown in Table 4.10 and on assumptions already described, the maximum content of total fatty acids, saturated fatty acids, unsaturated fatty acids with one double bond, and *n*-alkanes occurred at the flag leaf stage of growth, 53 days after seeding. However, their content declined thereafter to levels similar to or below of those shown at the early four-leaf unfolded stage. Interestingly, unsaturated fatty acids with $\geq$2 double bonds in soil solutions declined steadily from the four-leaf stage, 25 days after seeding until the hard grain stage, 102 days after seeding. Conversely,

Table 4.10 Ion intensities (II) for *m/z* assigned to fatty acids and alkanes in soil solutions obtained from the rhizosphere at four different growth stages of wheat

			II (counts × $10^2/\mu L^1$) at wheat growth stage			
m/z	**Fatty acids**	***n*-Alkanes**	**IF031**[a]	**IF093**[b]	**IF137**[c]	**IF196**[d]
46	n-C_1		40.23	43.75	47.33	30.99
58	n-$C_{2:1}$	n-C_4	110.52	77.44	60.72	50.23
60	n-C_2		95.63	80.70	145.55	138.41
72	$C_{3:1}$	n-C_5	49.65	55.83	53.83	45.51
74	n-C_3		47.38	50.83	86.19	108.85
86	$C_{4:1}$	n-C_6	94.17	61.76	56.65	65.88
88	n-C_4		32.15	38.36	30.39	23.60
100	$C_{5:1}$	n-C_7	45.63	54.45	36.46	36.00
102	n-C_5		40.64	41.27	46.15	57.91
114	$C_{6:1}$	n-C_8	56.29	55.94	70.16	123.36
116	n-C_6		26.05	34.49	43.94	68.80
128	$C_{7:1}$	n-C_9	52.99	94.03	84.54	101.61
130	n-C_7		21.46	36.58	27.90	21.23
142	$C_{8:1}$	n-C_{10}	33.50	49.35	47.47	68.93
144	n-C_8		43.75	55.89	56.42	116.73
156	$C_{9:1}$	n-C_{11}	44.69	54.00	46.94	19.64
158	n-C_9		35.97	45.44	42.74	26.55
170	$C_{10:1}$	n-C_{12}	33.91	51.74	49.77	45.37
172	n-C_{10}		59.65	58.51	43.69	44.87
182	$C_{11:2}$		62.80	71.90	49.77	55.98
184	$C_{11:1}$	n-C_{13}	49.56	54.42	39.10	35.15
186	n-C_{11}		30.16	96.56	72.20	68.70
196	$C_{12:2}$		67.74	71.95	48.53	63.32
198	$C_{12:1}$	n-C_{14}	59.83	78.66	82.30	63.19
200	n-C_{12}		42.07	61.48	82.30	57.98
210	$C_{13:2}$		97.93	97.53	66.30	91.09

Continued

Table 4.10 Ion intensities (II) for *m/z* assigned to fatty acids and alkanes in soil solutions obtained from the rhizosphere at four different growth stages of wheat—cont'd

			II (counts × $10^2/\mu L^1$) at wheat growth stage			
m/z	**Fatty acids**	***n*-Alkanes**	**IF031**	**IF093**	**IF137**	**IF196**
212	$C_{13:1}$	n–C_{15}	82.36	99.24	73.68	62.56
214	n–C_{13}		60.56	70.95	62.32	50.33
224	$C_{14:2}$		87.08	112.86	86.58	148.85
226	$C_{14:1}$	n–C_{16}	85.41	117.47	82.25	94.66
228	n–C_{14}		66.53	103.85	54.83	84.39
238	$C_{15:2}$		119.77	125.31	89.96	92.47
240	$C_{15:1}$	n–C_{17}	126.13	109.76	101.65	74.63
242	n–C_{15}		89.07	112.57	76.67	87.72
252	$C_{16:2}$		124.22	143.60	123.34	72.24
254	$C_{16:1}$	n–C_{18}	138.03	140.69	100.95	72.26
256	n–C_{16}		92.07	169.01	76.33	155.27
266	$C_{17:2}$		157.48	159.12	88.89	71.25
268	$C_{17:1}$	n–C_{19}	196.49	151.29	95.82	64.95
270	n–C_{17}		143.75	130.36	60.41	61.22
278	$C_{18:3}$		302.50	216.83	61.55	64.95
280	$C_{18:2}$		256.37	206.28	103.76	81.90
282	$C_{18:1}$	n–C_{20}	135.90	138.90	48.29	57.86
284	n–C_{18}		73.62	135.70	53.11	56.34
292	$C_{19:3}$		213.30	173.49	68.35	49.64
294	$C_{19:2}$		258.84	176.05	63.29	55.10
296	$C_{19:1}$	n–C_{21}	101.05	112.38	43.77	32.01
298	n–C_{19}		107.63	116.92	57.95	34.75
306	$C_{20:3}$		232.77	187.12	60.31	37.48
308	$C_{20:2}$		223.91	158.70	46.57	42.75
310	$C_{20:1}$	n–C_{22}	48.59	99.79	40.42	32.81
312	n–C_{20}		60.99	97.68	44.42	80.04

Table 4.10 Ion intensities (II) for *m/z* assigned to fatty acids and alkanes in soil solutions obtained from the rhizosphere at four different growth stages of wheat—cont'd

			II (counts $\times$ 10^2/μL^1) at wheat growth stage			
m/z	**Fatty acids**	***n*-Alkanes**	**IF031**	**IF093**	**IF137**	**IF196**
320	$C_{21:3}$		154.01	159.04	46.62	39.08
322	$C_{21:2}$		124.91	134.52	33.65	24.23
324	$C_{21:1}$	n-C_{23}	46.38	74.22	36.16	12.37
326	n-C_{21}		33.55	75.52	19.75	16.30
334	$C_{22:3}$		100.90	117.49	36.16	29.26
336	$C_{22:2}$		84.30	112.89	37.97	24.59
338	$C_{22:1}$	n-C_{24}	31.17	50.99	20.71	14.98
340	n-C_{22}		21.75	47.10	17.56	14.21
352	$C_{23:1}$	n-C_{25}	23.88	37.06	11.26	15.25
354	n-C_{23}		18.02	48.49	20.58	7.95
366	$C_{24:1}$	n-C_{26}	12.63	73.95	18.26	8.21
368	n-C_{24}		13.72	102.13	21.22	26.13
380	$C_{25:1}$	n-C_{27}	5.77	39.69	8.68	6.85
382	n-C_{25}		8.41	73.69	13.85	8.86
394	$C_{26:1}$	n-C_{28}	5.81	24.99	11.15	5.89
396	n-C_{26}		6.84	47.96	7.89	3.29
408	$C_{27:1}$	n-C_{29}	5.84	27.06	8.35	4.32
410	n-C_{27}		3.85	50.78	7.69	5.36
422	$C_{28:1}$	n-C_{30}	4.47	30.32	10.94	3.85
424	n-C_{28}		5.05	24.43	8.23	3.53
436	$C_{29:1}$	n-C_{31}	3.75	16.15	3.58	2.45
438	n-C_{29}		3.14	16.76	6.33	2.17
450	$C_{30:1}$	n-C_{32}	4.63	17.67	3.39	3.45
452	n-C_{30}		2.97	13.90	6.97	3.49
464	$C_{31:1}$	n-C_{33}	2.90	9.44	5.05	2.97
466	n-C_{31}		2.65	11.96	5.80	4.63

Continued

Table 4.10 Ion intensities (II) for *m/z* assigned to fatty acids and alkanes in soil solutions obtained from the rhizosphere at four different growth stages of wheat—cont'd

			II (counts × $10^2/\mu L^1$) at wheat growth stage			
m/z	**Fatty acids**	***n*-Alkanes**	**IF031**	**IF093**	**IF137**	**IF196**
478	$C_{32:1}$	n–C_{34}	3.28	6.56	5.73	2.42
480	n–C_{32}		5.55	9.53	3.80	2.21
492	$C_{33:1}$	n–C_{35}	2.42	8.87	3.44	2.59
494	n–C_{33}		3.40	4.74	2.68	2.50
506	$C_{34:1}$	n–C_{36}	4.86	11.85	3.57	1.96
508	n–C_{34}		4.47	7.53	5.15	1.96
520	$C_{35:1}$	n–C_{37}	4.84	8.57	3.95	1.91
522	n-C_{35}		2.40	7.19	3.80	2.17
534	$C_{36:1}$	n–C_{38}	2.97	18.09	5.66	1.87
536	n-C_{36}		2.39	12.81	2.83	1.83
548	$C_{37:1}$	n–C_{39}	2.28	10.22	5.54	2.06
550	n-C_{37}		2.46	5.27	2.71	1.88
562	$C_{38:1}$	n–C_{40}	2.13	5.01	3.44	1.48
564	n-C_{38}		2.49	2.56	2.40	1.30
			II for fatty acids (counts × $10^2/\mu L$)[e]			
Saturated			1354.60	2143.25	1363.66	1485.59
Unsaturated—1 double bond			860.85	1060.43	671.92	620.65
≥2 double bonds			2668.83	2424.68	1159.98	1064.53
Total fatty acids			4884.28	5628.36	3195.57	3170.76
			II for alkanes (counts × $10^2/\mu L$)			
Total alkanes			860.85	1060.43	671.92	620.65

[a]IF031 = four leaves unfolded (25 days after seeding).
[b]IF093 = flag leaf (53 days after seeding).
[c]IF137 = grain—early milk (72 days after seeding).
[d]IF196 = grain—dry seed (102 days after seeding).
[e]Assuming that of the II assigned to unsaturated fatty acids with one double bond, 50% are unsaturated fatty acids with one double bond and 50% are *n*-alkanes.

the abundance of saturated fatty acids $\leq n$-C_{10} in soil solutions consistently increased throughout the four growth stages.

4.8.2 Biochemistry and functions of fatty acids and n-alkanes in the rhizosphere

Fatty acids are important components of lipids in plants, animals, and microorganisms. The lipid matrix plays a fundamental role in the physical and chemical properties of biomembranes. Fatty acids are fundamental to energy production and storage, become parts of cell structures, and are used as precursors of hormones and other biologically active molecules (Harwood, 2005). Most fatty acids in nature form triglycerides by combination with glycerol. Acetyl-CoA carboxylase and fatty acid synthase are the two enzymes involved in the synthesis of fatty acids in plants, microorganisms, and other living cells (Hopwood, 1997). Fatty acid synthesis is closely linked to that of PKTs by polyketide synthases in prokaryotes and eukaryotes (Metz et al., 2001). Fatty acids constitute the essential part of triglycerides and wax esters, which are the major components of fats and oils (Bergé and Barnathan, 2005). Lipids are essential materials for the formation of cell and tissue membranes. When microbial or plant cells incorporate fatty acids into phospholipids, they are allocated into the cell membrane lipid bilayer, where they help create an impermeable barrier to water and polar molecules, thus separating the cell contents from the surrounding media.

In plant and other living cells, only a small proportion of the fatty acids occur in the free state, and most fatty acids are found esterified and associated with a variety of lipids. The most abundant fatty acid of green leaves is α-linolenic acid ($C_{18:2}$), followed by palmitic acid (n-C_{16}). In some roots, palmitic is the most abundant saturated fatty acid, and linoleic acid is the most abundant unsaturated fatty acid (Holman and Nichols, 1972; Mitchell et al., 1974). Wheat roots contain a pool of saturated and unsaturated C_{16} (i.e., palmitoleic) to C_{18} fatty acids equivalent to about 1% of the total root weight (Willemot et al., 1977). The content of saturated and unsaturated fatty acids at the tip of roots is between two to five times higher than 4 cm away from the tips (Mitchell et al., 1974). In root tips, the increase in linoleic acid level at low temperature is achieved directly by an increase in the amount of TaFAD3 protein encoded by the *TaFAD3* gene, and the temperature-dependent translational regulation of the *TaFAD3* gene, rather than its transcriptional regulation, contributes to modulation of the TaFAD3 protein accumulation (Horiguchi et al., 2000). In cell membranes, the content of some fatty acids, such as linoleic acid (18:1), increases dramatically in

the roots of winter wheat during the frost hardening period (Redshaw and Zalik, 1968). The high content of fatty acids in root tips and their diffusion or active transport help explain in part the presence of fatty acids in the soil solutions of wheat rhizosphere.

Fatty acids from C_7 to C_{14} added to aseptic wheat root tissues have been reported to be toxic, with maximal toxic effect exerted by C_9, C_{10}, or C_{11} fatty acids (Burström, 1950; Veldstra, 1947). Several fatty acids and alcohols with C_1 to C_4 were shown to promote cell elongation and the total growth of aseptically grown wheat roots, but their meristematic activity was inhibited at concentrations $>10^{-3}$ M (Gudjónsdóttir, 1966). The synthesis and exudation of low molecular weight organic acids from roots are an approach used by crops to tolerate environmental stress such as the presence of cadmium and nickel (Guo et al., 2007; Yang et al., 1997). Fatty acids from wheat can have allelopathic effects on other plants. Short-chain fatty acids affect crop development in soils with low redox potential (Lynch, 1978). Major allelopathic agents from wheat straw are acetic, propionic, and butyric acids, which inhibit seedling roots (Lynch et al., 1980).

The distribution and type of fatty acids in soil and soil solutions may be used as fingerprints to characterize the presence and role of fungi within soil microbial communities. For example, arbuscular mycorrhizal (AM) fungi have an enrichment signature of the fatty acid 16:1ω5, while ectomycorrhizal fungi are dominated by 18:2ω6,9 fatty acids. These signatures may be used as an indicator to study the mycelial biomass of these fungi in soils (Olsson, 1999). For fungal biomass estimation, the phospholipid fatty acids in membranes are suitable to describe soil microbial community structure (White et al., 1997). Noteworthy, soil bacteria also contain membrane phospholipid fatty acids and the ω-type fatty acids. The bacterial biosynthetic enzymes and genes involved in fatty acid synthesis and their inhibitors have been well studied (Zhang et al., 2006). Thus, truly representative characterization microbial community structures in ecosystems need to combine the use of fatty acid biomarkers together with genetic approaches for unambiguously elucidating their structure under different environments and crop management systems. The Py-FIMS data on free fatty acids found in the soil solution samples (Table 4.10) do not provide the necessary level of resolution to differentiate the types of soil mycorrhizal fungi. Our fatty acid and *n*-alkane data represent mostly pools of free compounds found in the soil solutions collected from the wheat rhizospheres.

Alkanes are produced by many living organisms such as plants, green algae, bacteria, or animals and are present at low concentrations in most soil and water environments (Han et al., 1969). Because alkanes are apolar molecules and

chemically very inert (Labinger and Bercaw, 2002), their metabolism by living cells poses challenges related to their low water solubility, their tendency to accumulate in cell membranes, and the energy needed to activate the molecule (Rojo, 2009). The genetics and biochemistry for the biosynthesis of *n*-alkanes have remained elusive, although they can be biosynthesized via three mechanisms. The first pathway involves the decarboxylation of fatty acids mediated by decarboxylases (Kaneshiro et al., 1999). The direct evidence for the presence of fatty acid decarboxylase in microorganisms, however, has not been elucidated (Ladygina et al., 2006). A second mechanism is by decarbonylation of fatty acids, which involves the reduction of fatty acids to a fatty aldehyde. The latter is then converted to alkane with the release of carbon monoxide through decarbonylation (Schirmer et al., 2010). The enzymes involved in this second pathway are an aldehyde-forming fatty acyl-CoA reductase and an aldehyde decarbonylase (Wang and Kolattukudy, 1995). A third pathway involves the reduction of a fatty alcohol to long-chain alkanes in a series of reactions. For example, hexadecanoic acid is converted into hexadecanal, which is then converted to hexadecanol and finally to hexadecane (Park, 2005). Microorganisms such as *Vibrio furnissi* and species of *Penicillium*, *Trichoderma*, *Aspergillus*, *Bacillus*, and some yeasts utilize the third pathway. Branched alkanes are mainly methylated on both ends of the molecule (Bird and Lynch, 1974). Cyclic hydrocarbons are mainly produced by photosynthetic bacteria, and long-chain linear hydrocarbons are predominant in fungal species (Ladygina et al., 2006). Hydrocarbons excreted by microorganisms into their surroundings are involved in lowering the disease resistance of plants and also act as antimicrobial agents (Graham and Linderman, 1980).

As shown in Table 4.10, the temporal decrease of unsaturated fatty acids and the increase in saturated fatty acids over the growing season of wheat indicate the preference of soil microorganisms for using these fatty acid as C sources for their metabolism. These results also confirm that in soil solutions and soil ecosystems, soluble unsaturated fatty acids are more reactive than saturated fatty acids. The greater content of unsaturated fatty acids (where some of the C-to-C are double or triple bonds) than saturated fatty acids (all C-to-C are single bonds) may also indicate a high probability for chemical reactions to occur between unsaturated fatty acids and microbial metabolites and/or other compounds from root exudates. Such chemical reactions may well contribute to the synthesis of phenolic lipids, helping form the central architectural unit of alkylaromatics proposed for HSs (Schnitzer and Monreal, 2011). Microorganisms also utilize alkanes and fatty acids as sources of C and energy (Wentzel et al., 2007). We hypothesize that the free unsaturated fatty acids and alkanes in soil

solutions, which appear to be mostly exuded by wheat roots, are rapidly used as sources of C and energy by the active soil microbial biomass. The microbial intracellular utilization of these compounds helps cells produce necessary metabolites and obtain their energy as adenosine triphosphate (ATP). Further, decarboxylation, decarbonylation, and reduction of fatty acids to fatty alcohols result in concomitant production of *n*-alkanes in soil solutions. Further research is required on (a) the chemical and microbial reactions of unsaturated fatty acids with other organic components of root exudates and soil solutions and (b) elucidating the ecological functions for *n*-alkanes and fatty acids in soil–crop rhizospheres.

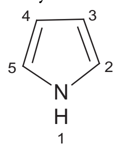
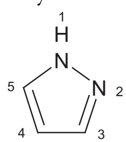
4.9. N-containing components of soil solutions

4.9.1 Py-FIMS analysis of N-containing components

N-components identified are listed in Table 4.11. A total of 94 N-components were identified: 82 were N-heterocyclics and 12 were other N-components. The N-heterocyclics were grouped into the following subclasses: substituted pyrroles; pyrazole and substituted pyrazoles and imidazoles; pyrazine and substituted pyrazines; pyridine and substituted pyridines; indole and substituted indoles; quinolines and benzoquinolines; carbazole and substituted carbazoles; and substituted phenyl pyridines. The other N-components were nitriles, benzonitrile, indazoles, and a few others. Substituents on the aromatic rings were methyl to decamethyls, acetyl, dihydroxy, amino, methoxy, propyl, and diketo groups.

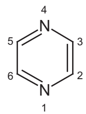
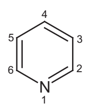
It is worth noting that the pyrolysis of N-containing compounds forms N-heterocyclics. For example, pyrolysis of porphyrin from chlorophyll forms substituted pyrroles and that of chitin produces pyridine as well as alkyl pyridines (van der Kaaden et al., 1984). The pyrolysis of hydroxy-amino acids produces pyrazine (Chiavari and Galletti, 1992) and that of tryptophan can produce indoles. Therefore, confirmation of the presence of the N-containing components in the soil solutions as reported herein by Py-FIMS needs complementary analyses by other analytical methods such as N K-edges XANES (Jokic et al., 2004) and liquid chromatography electrospray ionization mass spectrometry–mass spectrometry (LC-ESI-MS/MS) (McRae and Monreal, 2011). N-heterocyclics can also be formed from the reaction of phenols and quinones with proteins, peptides, amino acids, and NH_3 (Schulten and Schnitzer, 1998). Of special interest are the studies on the formation of complex N-containing polymers from the chemical reaction of phenols with NH_3 (Flaig et al., 1975).

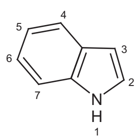
Table 4.11 Ion intensities (II) for *m/z* assigned to nitrogen-containing compounds in soil solutions obtained from the rhizosphere at four different growth stages of wheat

m/z	Structure	Identity	II (count × 10^2/μL) at wheat growth stage IF031[a]	IF093[b]	IF137[c]	IF196[d]
		Substituted pyrroles				
81	Pyrrole 	Methylpyrrole	29.29	33.05	54.87	76.14
83		Hydroxypyrrole	43.91	47.79	59.89	48.08
109		2-Acetylpyrrole	24.45	36.69	46.44	21.50
186		Diketopyrrole	30.16	96.58	72.20	68.70
Subtotal			127.81	214.09	233.40	214.42
		Pyrazole and substituted pyrazoles and imidazoles				
68		Pyrazole	27.26	32.61	41.28	21.15
82		Methylpyrazole	28.96	53.09	46.79	42.67
84		Hydroxypyrazole	78.58	116.42	127.93	146.93
96	Pyrazole 	Dimethylpyrazole	69.24	62.63	84.51	106.77
110		1,3,5-Trimethylpyrazole	52.46	90.57	96.01	111.62
124		1-Ethyl-3,5-dimethylpyrazole	52.84	53.80	57.63	54.48
138		Pentamethylpyrazole	67.90	73.76	63.91	74.78
166		Tetramethyl-propylpyrazole	57.92	66.64	54.82	62.41
180		Tetramethyl-butylpyrazole	73.57	78.86	56.58	76.47
222		Tetramethyl-heptylpyrazole	143.63	153.16	96.27	66.69
99		4-Methylimidazole	110.77	125.13	89.64	81.69
130		2-Ethyl-4,5-dihydroxy-imidazole	21.46	36.58	27.90	21.23
Subtotal			784.64	943.25	843.27	866.74

Continued

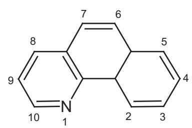
Table 4.11 Ion intensities (II) for *m/z* assigned to nitrogen-containing compounds in soil solutions obtained from the rhizosphere at four different growth stages of wheat—cont'd

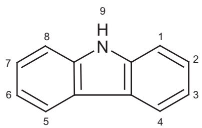
			II (count × 10^2/μL) at wheat growth stage			
m/z	**Structure**	**Identity**	**IF031**	**IF093**	**IF137**	**IF196**
		Pyrazine and substituted pyrazines				
80		Pyrazine	28.76	29.02	35.50	24.46
108		2,3-Dimethylpyrazine	37.20	43.79	47.17	38.17
136	Pyrazine	Tetramethylpyrazine	62.26	56.48	53.68	50.83
152		Methoxy-propylpyrazine	57.62	75.78	58.98	75.74
178		Pentamethyl-ethylpyrazine	141.92	135.99	90.98	98.14
192		Pentamethyl-propylpyrazine	70.95	88.69	57.41	76.62
206		Pentamethyl-butylpyrazine	90.85	98.79	60.33	105.51
220		Pentamethyl-pentylpyrazine	65.25	136.63	53.94	77.51
Subtotal			554.81	665.17	457.99	546.98
		Pyridine and substituted pyridines				
79		Pyridine	26.12	26.63	27.59	18.12
93	Pyridine	Methylpyridine	20.26	26.71	40.46	18.58
94		Aminopyridine	36.45	40.22	57.38	31.19
95		3-Hydroxypyridine	24.94	32.88	35.57	21.19
104		3-Nitrile pyridine	26.32	22.86	33.93	28.93
107		Dimethylpyridine	20.68	33.32	42.02	19.61
111		Dihydroxypyridine	30.50	39.33	37.04	30.27

121		Trimethylpyridine	19.45	26.85	28.58	17.73
135		Tetramethylpyridine	30.88	34.33	29.73	23.44
149		Pentamethylpyridine	33.73	41.41	34.31	27.25
153		Hydroxy-acetoxypyridine	26.81	34.17	29.18	29.05
163		Hexamethylpyridine	24.77	44.54	40.85	33.85
177		Pentamethyl-ethylpyridine	21.50	34.34	27.84	24.66
Subtotal			342.41	437.59	464.48	323.87
		Indoles and substituted indoles				
117		Indole	22.69	31.35	29.98	38.95
131		3-Methylindole	16.37	25.99	22.36	24.91
145	Indole	2,6-Dimethylindole	30.26	31.75	41.32	26.95
159		1,2,3-Trimethylindole	36.58	32.72	41.18	18.50
161		Indolethanol	33.87	38.81	29.72	17.90
173		Methyl-acetylindole	39.66	43.51	27.44	17.42
175		Indole acetic acid	22.85	33.14	30.65	23.75
187		Ethyl-acetylindole	21.49	42.25	38.47	27.48
201		Hexamethylindole	17.47	48.08	72.95	27.52
243		Hexamethyl-propylindole	44.55	122.72	68.06	44.20
Subtotal			285.79	450.32	402.03	267.56

Continued

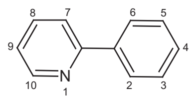
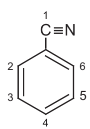
Table 4.11 Ion intensities (II) for *m/z* assigned to nitrogen-containing compounds in soil solutions obtained from the rhizosphere at four different growth stages of wheat—cont'd

			II (count × 10^2/μL) at wheat growth stage			
m/z	**Structure**	**Identity**	**IF031**	**IF093**	**IF137**	**IF196**
		Quinolines and benzoquinolines				
133		Isoquinoline	17.81	32.19	31.13	19.95
157		Ethylquinoline	19.81	36.80	26.54	22.56
171		Propylquinoline	23.18	32.43	26.77	28.73
179	Benzoquinoline	Benzoquinoline	35.18	42.05	26.76	25.88
185		Butylquinoline	26.25	35.72	33.12	25.41
193		Methylbenzoquinoline	21.49	43.63	25.54	28.79
207		Dimethylbenzoquinoline	23.03	42.76	25.30	23.99
221		Trimethylbenzoquinoline	28.08	53.63	26.19	24.54
235		Tetramethylbenzoquinoline	23.80	56.07	48.27	32.30
249		Pentamethylbenzoquinoline	28.95	105.54	31.47	31.33
263		Hexamethylbenzoquinoline	46.34	57.31	43.86	31.09
277		Heptamethylbenzoquinoline	46.28	78.12	30.00	20.69
291		Octamethylbenzoquinoline	48.36	51.11	24.85	14.66
Subtotal			379.85	612.23	399.80	328.82

		Carbazole and substituted carbazoles				
167	Carbazole 	Carbazole	25.01	47.41	33.83	23.46
181		Methylcarbazole	22.76	32.29	26.58	28.46
195		Dimethylcarbazole	23.83	52.36	36.70	30.66
209		Trimethylcarbazole	38.31	56.59	37.32	29.41
223		Tetramethylcarbazole	42.06	71.49	50.61	29.06
237		Pentamethylcarbazole	28.37	50.97	30.13	27.30
251		Hexamethylcarbazole	38.25	58.85	56.15	46.25
265		Heptamethylcarbazole	38.83	55.77	36.26	28.37
279		Octamethylcarbazole	90.31	90.55	50.32	25.31
293		Nonamethylcarbazole	60.76	84.13	31.67	21.27
307		Octamethyl-propylcarbazole	68.63	77.51	29.39	12.19
321		Octamethyl-butylcarbazole	32.93	79.23	33.35	15.57
335		Octamethyl-pentylcarbazole	28.71	41.72	17.92	7.70
349		Octamethyl-hexylcarbazole	26.06	64.46	9.39	8.00
Subtotal			564.82	862.83	479.6	333.02

Continued

Table 4.11 Ion intensities (II) for *m/z* assigned to nitrogen-containing compounds in soil solutions obtained from the rhizosphere at four different growth stages of wheat—cont'd

			II (count × 10^2/μL) at wheat growth stage			
m/z	**Structure**	**Identity**	**IF031**	**IF093**	**IF137**	**IF196**
		Substituted phenylpyridines				
281		Nonamethylphenylpyridine	82.13	67.60	35.77	38.55
295		Decamethylphenylpyridine	73.87	75.67	24.93	19.79
309	Phenylpyridine	Nonamethyl-propylphenylpyridine	49.55	81.11	24.66	20.94
323		Nonamethyl-propylphenylpyridine	46.11	53.37	15.56	13.07
337		Nonamethyl-butylphenylpyridine	19.39	53.23	19.36	6.81
351		Nonamethyl-pentylphenylpyridine	17.69	33.66	9.32	13.90
365		Nonamethyl-hexylphenylpyridine	16.62	43.87	18.30	11.88
379		Nonamethyl-heptylphenylpyridine	9.92	50.02	8.81	4.45
Subtotal			315.28	458.53	147.27	124.76
		Other N-compounds				
69		2-Methylpropanenitrile	111.98	146.54	66.05	41.63
87	Nitriles R—C≡N	Formylacetamide	53.44	82.30	43.76	33.92
91	Benzonitriles	Cyanocyclopentadiene	23.84	26.51	28.88	20.53
97		4-Methylpentanenitrile	31.98	42.17	44.29	55.25
98		2,5-Pyrrolidinedione	90.48	91.45	116.72	152.87
103		Benzonitrile	41.91	38.32	26.08	26.50
113		Amino-methylfuranone	60.11	66.83	52.24	70.90

119	4-Hydroxybenzonitrile	32.88	41.95	33.71	16.70
122	Heptanedinitrile	66.00	79.29	41.93	43.21
129	1-Piperazineethanamine	20.12	41.25	30.27	28.74
132	5-Methyl-1H-indazole	27.88	43.28	43.87	42.13
137	Amino-benzene-ethanol	19.42	20.56	28.11	23.90
Subtotal		580.04	684.66	555.91	556.28
		N-containing compound subclasses			
Substituted pyrroles		194.21	214.09	216.33	346.28
Pyrazole and substituted pyrazoles and imidazoles		784.64	943.25	843.27	866.74
Pyrazine and substituted pyrazines		554.81	665.17	457.99	546.98
Pyridine and substituted pyridines		342.41	437.59	464.48	323.87
Indoles and substituted indoles		285.79	450.32	402.03	267.56
Quinolines and benzoquinolines		456.93	726.35	492.21	403.45
Carbazole and substituted carbazoles		487.74	748.71	387.19	258.39
Substituted phenylpyridines		315.28	458.53	147.27	124.76
Other N-compounds		580.04	684.66	555.91	556.28
Total N-compounds		4001.85	5328.67	3966.68	3694.31

[a]IF031 = four leaves unfolded (25 days after seeding).
[b]IF093 = flag leaf (53 days after seeding).
[c]IF137 = grain—early milk (72 days after seeding).
[d]IF196 = grain—dry seed (102 days after seeding).

Table 4.11 indicates that the growth stage of wheat influenced the abundance of N-compounds in soil solutions. Overall, the maximum content of N-containing components in solutions occurred at the flag leaf stage of growth, 53 days after seeding; and their content declined thereafter to levels similar to or below those shown in solutions at the early four-leaf unfolded growth stage, 25 days after seeding. In particular, effects of the four stages of wheat growth on the concentrations of the N-heterocyclic subgroups were as follows: increases from the first to the second growth stage and then decreases were observed for pyrazoles, pyrazines, indoles, quinolines and benzoquinolines, carbazoles, phenylpyridine, nitriles, and benzonitriles. Increases from the first to the third growth stages and then decreases were observed for substituted pyrroles, pyridines, and substituted pyridines. Noteworthy, the temporal dynamics and maximum content of N-containing compounds in soil solutions coincided with those shown by basic amino acids, lignin monomers and dimers, *n*-alkylbenzenes, flavonoids, fatty acids, and *n*-alkanes during the flag leaf stage, 53 days after seeding.

The most abundant N-containing components of solutions were 2-methylpropanenitrile (m/z 69), 4-methylimidazole (m/z 99), pentamethyl-ethylpyrazine (m/z 178), and tetramethyl-heptylpyrazole (m/z 222), whose abundances ranged from 11,000 to 15,000 counts/μL. All other m/z values showed abundances $<$10,000 counts/μL during the growing season of wheat.

The relatively high content of the N-containing compounds in soil solutions parallels that found in earlier studies with whole soil samples. Analysis of whole soil samples by Py-FIMS has indicated that heterocyclic-N accounts for about 35% of the soil organic N on the basis of GC/MS, Cp Py-GC/MS, and Py-FIMS sample analyses (Schulten and Schnitzer, 1998). According to Vairavamurthy and Wang (2002), heterocyclic-N constitutes up to 30% of total N in HSs and sediments. The same authors proposed that abiotic formation of heterocyclic-N compounds may also occur during early stages of organic matter transformations. Further convincing evidence for the existence of heterocyclic N was presented in a study of unaltered soil samples using N K-edge XANES (Jokic et al., 2004).

4.9.2 Biochemistry and functions of N-containing compounds in the rhizosphere

In nature, N-heterocyclics perform a variety of biological functions, such as coordinating and controlling the metabolism in all cells and tissues, as these molecules were selected by nature to be the hub of metabolism. The vast majority of biochemical reaction sequences in living cells involve a

N-heterocyclic compound as substrate, product, or coenzyme (Brown, 1998). Heterocyclic-N compounds are widely distributed in plants, animals, and soil organisms (Sasse et al., 2003). Units of heterocyclic-N are basic structural components of nucleotides in DNA and RNA (Alberts et al., 2002; McMurry and Begley, 2005), ATP, the coenzymes nicotinamide adenine dinucleotide (NAD) and nicotinamide adenine dinucleotide-phosphate (NADP), chlorophyll (Brown, 1998; von Wettstein et al., 1995), biologically active alkaloids (Salas and Corcuera, 1991), antibiotics (Turiel et al., 2006), and many aromatic and aliphatic PKTs (Das and Khosla, 2009; Nakano et al., 2009). Heterocyclic-N components are intricate molecular structural pieces contributing to the diversity of PKTs in nature (Hertweck, 2009), and of other chemical components of biological importance. Heterocyclic-N components can be used as C and N sources by microorganisms and may exist as electron carriers such as NAD (P)H and flavine nucleotides, and as constituents of energy-storage molecules (ATP, GTP) (Fetzner, 1998). Nitrogen heterocycles are well-known metal chelators and can easily deactivate various metalloenzymes (Seo et al., 2009).

4.9.2.1 Biochemistry and functions of pyrroles in the rhizosphere

Pyrrole groups are found in primary metabolites and in a large variety of secondary metabolites (Lautru et al., 2012). Pyrroles can be produced via six different biosynthetic pathways (Siebenberg et al., 2011) from several precursors such as amino acids, small size organic acids, or other compounds (Walsh et al., 2006). Its five-member ring plays important functions in biological systems, helps form hydrogen bonds, coordinates metals, and provides stacking interactions between aromatic rings. Pyrrole is a key constituent of the bicyclic indole side chain of L-tryptophan residues in proteins and is present in a wide range of natural products (Walsh et al., 2006). Because of its ability to bind to DNA, several of its derivatives have anthelmintic, antifungal, and antibacterial properties.

4.9.2.2 Biochemistry and functions of pyrazoles in the rhizosphere

Pyrazole, another heterocyclic-N compound in soil solutions, is synthesized in plants, microbial cells, and animals. Pyrazole in some plant species is derived from 1,3-diaminopropane and histidine, and it can occur extensively in free state of living cells (Brown and Diffin, 1990). Many pyrazole alkaloids are synthesized by plants as defensive compounds and excreted into their surroundings (Polya, 2003). Examples of naturally occurring pyrazoles include pyrazofurin and formycin A, which have antifungal and antiviral activities produced by the mold *Streptomyces lavendulae and S. candidus* (Koyama

et al., 1966). Another example of a fused pyrazole is withasomnine, an alkaloid found in roots of solanaceaes, mushrooms, trees, and oats (Polya, 2003; Schröter et al., 1966). A number of synthetic pyrazole derivatives are also used as herbicides and fungicides (Brown, 1998; Brown and Diffin, 1990).

4.9.2.3 Biochemistry and functions of pyrazines in the rhizosphere

Pyrazines occur frequently in plants, bacteria, and animals, and are mostly present as substituted pyrazines (Müller and Rappert, 2010). These compounds are produced in several bacteria, with 2,5-diisopropylpyrazine as a major compound (Beck et al., 2003; Schulz and Dickschat, 2007). Some of these bacterial compounds are volatile due to their low vapor pressure and odor-producing substances (Dickschat et al., 2010). A total of 19 pyrazine metabolites were produced by *Paenibacillus polymyxa*, a plant growth-promoting soil bacteria living in rhizospheres (Beck et al., 2003). Wagner et al. (1999) identified 70 different alkylpyrazines in nature. Very little information exists on the bacterial degradation of pyrazines, but it has been suggested that they are converted via oxidation of the methyl group, hydroxylation of the alkyl moieties, and also dihydroxylation with ring cleavage by an oxidase to form glycine (Mattey and Harle, 1976).

Pyrazines can be used as C, N, and energy sources by microorganisms in terrestrial ecosystems. For example, the compound 2,3-diethyl-5-methylpyrazine, the second most abundant heterocyclic-N compound found in the wheat soil solution, can be used as the sole carbon and energy source by soil *Mycobacterium poriferae* (Rappert et al., 2006). Interestingly, the *M. poriferae* strain does not grow on complex media like tryptic soy broth, Luria-Bertani broth, or nutrient broth or on simple carbon sources like glucose, acetate, oxoglutarate, succinate, or citrate, indicating a high specificity and affinity of *M. poriferae* for this specific substituted pyrazine.

4.9.2.4 Biochemistry and functions of pyridines and phenylpyridines in the rhizosphere

In nature, pyridines are mostly found as derivatives forming part of building blocks for many biomolecules with a large chemical diversity and functions. Examples of these biomolecules are the pyridine nucleotides (i.e., NAD, NADP), pyridoxal, and niacin in vitamins B_6 and B_3, respectively. Pyridine and its derivatives have important cell functions not only in the processes of primary metabolism but also in the production of the secondary metabolites such as alkaloids. Although the biosynthesis of pyridines is not fully understood, some publications report on pathways in some living cells. For example, the

aerobic metabolism of tryptophan by yeasts, molds, and bacteria supplies the C and N to form the pyridine ring in NAD (Foster and Moat, 1980). Quinolinic acid is a central precursor of pyridine ribonucleotide pools in living cells, where N in quinoline comes from aspartic acid and the C moiety comes from glycerol (Begley et al., 2001; Yang and Waller, 1965). In *Escherichia coli* and *Mycobacterium tuberculosis*, niacin is synthesized from glyceraldehyde-3-P and aspartate; in *Zea mays*, it is produced by oxidation of tryptophan (Tarr and Arditti, 1982). Alkaloids, heterocyclic compounds with a great diversity of pyridine ring structures, show many different biosynthetic enzymatic pathways. In spite of their metabolic diversity, the biological precursors of most alkaloids can be amino acids, or alternatively, they can be produced by transamination reactions (Aniszewski, 2007).

Closely related N-heterocyclic compounds are phenylpyridines and dipyridines, which act as bioactive compounds. Some plant phenylpyridine alkaloids, similar to the phenylpyridines found in the soil solution, are synthesized from nicotinic acid via *N*-methyl-3-cyanopyridine (Brown, 1998). In the wheat soil solution study, all phenylpyridines were methyl substituted (Table 4.11). Methylated phenylpyridines, such as the coprismycins A and B, are produced by soil microorganisms such as *Streptomyces* sp. living in association with insects (Kim et al., 2011; Poulsen et al., 2011). The roles of symbiotic partners and the symbiotic tightness between host insects and their associated microbes in soils or other ecosystems have not been established yet (Kim et al., 2011). Data from the wheat soil solution study together with published information indicate that further research is warranted on the potential role and function of pyridines and phenylpyridines produced by plants and microorganisms in soil habitats, especially those functions related to processes of soil nitrogen cycling, synthesis of soil HSs, and the roles of bioactive compounds in soil microbiota–insect symbiosis.

4.9.2.5 Biochemistry and functions of indoles in the rhizosphere

Indoles are heterocyclic-N compounds found in plants and microorganisms. Indoles are the building blocks of plant and bacterial hormones, alkaloids, and enzymes. The precursor of all indoles is tryptophan (Van Onckelen et al., 1986). The enzyme indole-3-glycerol phosphate lyase catalyzes the formation of free indole (Frey et al., 2000). Plants and many beneficial and pathogenic soil bacteria use indoles as precursor of the hormone auxin or indole-3-acetic acid (IAA) (Allan, 1977; Patten and Glick, 1996). Up to 80% of bacteria isolated from the rhizosphere of wheat and rye produce IAA (Leinhos and Vacek, 1994). Soil bacteria may modify the endogenous root auxin level to an optimal

or supra-optimal level for inducing plant growth. The biosynthetic pathways, the structure and regulation of the genes involved, the reasons why microbes produce auxin, and the mechanisms by which bacterial auxin influences plants are discussed by Patten and Glick (1996). The whole maize plant and a variety of other plant species synthesize and release indole and terpenoids in response to herbivore attacks. The production of indole in plants is triggered by the fatty acid derivative *N*-(17-hydroxylinolenoyl)-L-glutamine (Frey et al., 2000). Terpenes are synthesized by terpene synthase or cyclases which are encoded by genes upregulated by insect damage (Lin et al., 2008). In plants, a mix of terpenoids and indoles is synthesized as an indirect defense mechanism to attract *Cotesia marginiventris*, a parasitic wasp that attacks larvae of several species of Lepidoptera (Turlings et al., 1990, 1993).

The indole moiety is also contained in a number of alkaloids. Based on their biosynthesis, there are two types of indole alkaloids, isoprenoids and non-isoprenoids. Strigolactones, which are a large class of isoprenoids derived from carotenoid catabolism, are produced by plants and microbes and exuded from the roots of many plant species (Floss et al., 2008). They induce the hyphal branching of symbiotic AM fungi and also of root parasitic seeds (Yoneyama et al., 2009). The presence of strigolactones or their derivatives in soil matrices has not been investigated by Py-FIMS or other analytical techniques. Indoles and several substituted indoles were present in our soil solutions, including m/z 175, IAA, the growth hormone that is present in roots and bacteria.

4.9.2.6 Biochemistry and functions of quinolines and their derivatives in the rhizosphere

Quinolines and their alkyl, aryl, and alkylquinolines and alkylquinolinone derivatives are biosynthesized by species of plants and microorganisms (da Silva et al., 2007). Many quinolines are bioactive alkaloids and are highly soluble in water. Quinolines are also the building blocks of quinoproteins and coenzymes in a variety of bacteria. Examples of quinoproteins are dehydrogenase, alcohol dehydrogenase, and methanol dehydrogenase (Goosen et al., 1992). Most research on quinoline-degrading microorganisms has been conducted due to their mobility in the environment and for their antimicrobial activities in medicine (Ghorab et al., 2001). Quinoline and their derivatives can be used as the carbon, energy, and nitrogen sources by many bacteria in soils and water systems (Schwarz et al., 1988). Quinolines and alkylquinolines in higher plants and microorganisms can be derived from tryptophan; quinolones from glycine and a PKT. Alkylquinolines and alkylquinolones are well known as typical alkaloids of three Proteobacteria

and three Actinobacteria; the genus *Pseudomonas* yielded the majority (46%) of the total number of alkaloids reported (da Silva et al., 2007). Quinolactacins, in which the second nitrogen of the quinolin is derived from L-valine or L-isoleucine, have been recently reported to occur only in the soil fungus *Penicillium* (da Silva et al., 2007).

All microbial aerobic degradation pathways of quinoline (Q) produce 2-hydroxyquinoline, which tautomerizes to the lactam 2-quinolinone. One pathway proceeds via 2,6-dihydroxy-Q and 5-hydroxy-6-(3-carboxy-3-oxopro-penyl)-2-pyridone, which decomposed to pyran-2-one-[3,2b]-6-pyridine. A second pathway proceeds via 2,8-dihydroxy-Q, 8-hydroxycoumarin, and 2,3-dihydroxyphenyl-propionic acid (Miethling et al., 1993). A third pathway indicates the production of 5,6-*cis*-dihydrodiols, 3- and 8-hydroxy-Q, and subsequently anthranilic acid (Boyd et al., 1983). Anthranilic acid is an important precursor of quinoline-derived alkaloids in microorganisms (da Silva et al., 2007). The few investigations that have described the microbial metabolism of quinolines under anaerobic conditions all involved the initial hydroxylation at position 2 (Liu et al., 1994). Oxygenated quinolines were partially transformed into *N*-methyl, *C*-methyl, and *O*-methyl derivatives under methanogenic conditions (Pereria et al., 1987). More than 10,000 colonies of quinoline-degrading microorganisms were isolated from an oil-contaminated soil (Lin et al., 2011). Quinoline and 2-hydroxyquinoline can be used as the carbon, energy, and nitrogen source by *Rhodococcus* sp., and its degradation results in the release of ammonia and pigmented compounds into the growth medium (O'Loughlin et al., 1996). Many of the quinolines found in the wheat soil solution samples were of the benzoquinoline types found in higher plants (da Silva et al., 2007).

4.9.2.7 Biochemistry and functions of carbazoles in the rhizosphere

Carbazole and its derivatives are found in plants and microorganisms and exhibit a broad range of molecular frameworks and functional groups. Many of these natural compounds are bioactive alkaloids. Generally, the plant alkaloid carbazoles feature a C-1 substituent at C-3 in higher plants or C-2 in lower plants (the substituent usually a methyl group or its oxidized equivalents) (Schmidt et al., 2011). Conversely, carbazoles in microorganisms usually lack the carbon substituent at C-3. Several biosynthetic pathways have been proposed for carbazole but all of them lack experimental evidence (Schmidt et al., 2011). A proposed pathway in higher plants may be by oxidation of the methyl substituent (Knölker and Reddy, 2002). Another may be the "anthranilic acid pathway," which proceeds via the 3-prenylquinolone, which

represents the most widely accepted pathway for carbazole alkaloids in higher plants (Leistner and Zenk, 1968). Prenylated or polyprenylated indoles have also been suggested to be precursors of carbazole (Chakraborty and Roy, 2003). Depending on where carbazoles are formed, the terpenoid carbon atoms may derive from mevalonic acid or methylerythritol phosphate. Biogenetic studies on carbazole alkaloids from microbial sources indicated that L-tryptophan is a precursor for the carbazole carbazomycin B, where L-tryptophan provides the indole moiety as well as C-3 and C-4 of the hexasubstituted benzene ring. A recent review by Schmidt et al. (2011) offers a detailed discussion of other possible pathways for carbazole formation.

Carbazole can be degraded by many species of soil bacteria. For example, species of *Acromobacter*, *Arthrobacter*, *Chryseobacterium*, and *Xanthomonas* catabolically decompose carbazole (Seo et al., 2009). Guo et al. (2008) isolated a stable carbazole-degrading microbial consortium from sediments that consisted of *Chryseobacterium* sp. NCY and *Achromobacter* sp. NCW. Seo et al. (2006) reported carbazole degradation in *Arthrobacter* sp. P1-1. Although the catabolism of carbazole is not clearly understood, carbazole catabolism appears to be controlled by mono-, di-, and multiple dioxygenases at carbons 3 and 4 (Liang et al., 2006; Resnick et al., 1993). These initial steps result in the formation of corresponding diols followed by ring fission (Grifoll et al., 1995; Ouchiyama et al., 1993). In contrast to bacteria, filamentous fungi can introduce one or several hydroxyl groups in a ring of aromatic compounds (Cerniglia, 1992). Microorganisms can utilize carbazole as the source of carbon and nitrogen such as reported for *Enterobacter* sp. (Singh et al., 2011). In contrast to bacteria, filamentous fungi can introduce one or several hydroxyl groups in a ring of aromatic compounds. In the *Aspergillus flavus* VKM F-1024 fungi, the compound 3-hydroxycarbazole was revealed as a major bioconversion product, and 1-hydroxy- and 2-hydroxycarbazoles were observed as minor products. In the presence of another N-heterocyclic, 1-benzoylindole, the hydroxylation position shifted toward preferable accumulation of 2-hydroxycarbazole and the formation of 2,6- and 2,7-dihydroxycarbazoles. At the conversion of *N*-acetyl- and *N*-benzoylcarbazoles, carbazole was found to be the major product, while 1-, 2-, and 3-monohydroxycarbazoles were formed in small amounts (Lobastova et al., 2004).

4.9.2.8 Biochemistry and functions of other N-components in the rhizosphere

In the wheat rhizosphere soil solution study, the content of N-components (mostly N-heterocyclics) varied from 16% to 22% of the TII depending on the growing stage of wheat (Table 4.11). The content of heterocyclic-N

compounds represented 85–87% of all N-containing compounds. All N-containing compounds found in the wheat soil solutions samples are biosynthesized by plants, microorganisms, and insects, and are also utilized as C, energy, and N sources by different bacteria (Conn, 1980, 1981; Müller and Rappert, 2010; Rappert et al., 2006). The content of the other N-compounds, such as nitriles and benzonitriles, ranged from 12% to 15% of all N-containing compounds identified in the soil solutions of wheat rhizospheres (Table 4.11). For example, 2-methylpropanenitrile, the most abundant nitrile in the wheat rhizosphere soil solutions, is the intermediate precursor for cyanogenic glycosides, secondary metabolites synthesized mostly in higher plants and insects (Conn, 1981; Davis and Nahrstedt, 1987). A soil *Pseudomonas* sp. (S1) utilizes nitriles, such as 2-methylpropanenitrile (m/z 69), as carbon and nitrogen sources. The enzyme nitrilase from the *Pseudomonas* sp. (S1) strain catalyzes the direct hydrolysis of organic cyanides (C–N) to their corresponding carboxylic acids and ammonia. Nitrilase is induced by both aliphatic and aromatic nitriles. This enzyme also catalyzes the hydrolysis of acetonitrile, adiponitrile, benzonitrile, butyronitrile, glutaronitrile, phenylacetonitrile, succinodinitrile, and potassium cyanide (Dhillon and Shivaraman, 1999).

Benzonitrile, which was another N-heterocyclic found in the wheat soil solutions, can serve as C, energy, and N sources to various soil microorganisms. Nitrilases utilizing benzonitrile as a preferred substrate have been purified from *Nocardia*, *Fusarium solani*, and *Arthrobacter* sp., and its metabolism release ammonia (Collins and Knowles, 1983; Kobayashi et al., 1989).

A library of spectral features for using N K-edge XANES spectroscopy in soil and environmental samples has been provided for mineral-N and several organic N-containing compounds such as heterocyclic-N and nitriles (Leinweber et al., 2008).

4.9.2.9 Future research on N-containing components in soil solutions

Future research is required on the biosynthesis and chemistry of many of the N-containing compounds (i.e., heterocyclic, nitriles, and polyamides) *in vivo* soil–plant systems and associated microorganisms in the rhizosphere. Such research studies would clarify differences in the pathways based on their precursors (i.e., amino acids, anthranilic acid) in plants and soil microorganisms. The release of N-heterocyclics into soil solutions and their use as substrates for the microbial production of soil mineral-N for crop uptake is unknown but need to be elucidated. Research is also warranted on the roles of N-heterocyclics in plant growth regulation and control of plant pathogens as alkaloids and PKT bioactive compounds.

4.10. Steroids and sterols in the soil solution

4.10.1 Py-FIMS analysis of steroids and sterols

Table 4.12 lists 13 steroids and sterols which we identified in the four soil solutions. The most abundant *m/z* values were produced by cholestadiene (*m/z* 368) and cholesterol (*m/z* 386). Overall, the maximum concentration of all steroids and sterols occurred at the flag leaf stage, 53 days after seeding wheat; thereafter their content decreased to levels similar to those observed during the early four-leaf stage, 25 days after seeding. The temporal pattern

Table 4.12 Ion intensities (II) for *m/z* assigned to sterols and steroids in soil solution obtained from the rhizosphere at four different growth stages of wheat

		II (count × 10^2/μL) at wheat growth stage			
m/z	**Identity**	**IF031**[a]	**IF093**[b]	**IF137**[c]	**IF196**[d]
		Sterols			
386	Cholesterol	32.13	122.01	18.91	6.68
396	Ergosterol	6.84	47.96	7.89	3.29
400	Campesterol	16.51	55.47	18.78	3.90
412	Stigmasterol	9.94	55.18	5.52	6.13
414	β-Sitosterol	15.77	48.33	5.73	6.53
416	Dehydro-β-sitosterol	12.88	24.17	5.88	5.84
430	α-Tocopherol	8.17	28.63	6.62	7.02
	Subtotal	102.24	381.75	69.33	39.39
		Steroids			
368	Cholestadiene	13.72	102.13	21.22	26.13
370	Cholestene	15.29	62.66	18.52	10.61
394	Stigmastatriene	5.81	24.99	11.15	5.89
398	Stigmastene	13.19	52.02	13.27	8.37
410	Stigmastadienone	3.85	50.78	7.69	5.36
426	D:A-Friedooleanan-3-one	4.25	17.61	4.40	2.74
	Subtotal	56.11	310.19	76.25	59.10
Total		158.35	691.94	145.58	98.49

[a]IF031 = four leaves unfolded (25 days after seeding).
[b]IF093 = flag leaf (53 days after seeding).
[c]IF137 = grain—early milk (72 days after seeding).
[d]IF196 = grain—dry seed (102 days after seeding).

and maximum content of steroids and sterols were similar to those observed for N-containing compounds and other classes of chemical compounds as identified in Section 4.9.1.

4.10.2 Biochemistry and functions of steroids and sterols in the rhizosphere

Sterols and steroids occur in plants, algae, most fungi, protozoa, and some animals. Insects that make 80% of the animal species do not synthesize sterols (Svoboda and Weirich, 1995). Most prokaryotes (i.e., bacteria, cyanobacteria) do not synthesize sterols but often produce instead sterol-like molecules such as the hopanoids (Rohmer et al., 1984). A few bacterial species, however, can produce sterols (Pearson et al., 2003). Sterols are found as a mixture of several major biomolecules in free forms (the majority 3-β-hydroxyl and sterified (steryl esters and steryl glucosides)). The major components of sterols in plants are 64% sitosterol, 11% 24-methylcholesterol, 6% stigmasterol, 3% isofucosterol, and 2% ergosta-5,22E-dien-3β-ol, a sterol only present in brassicaceae (Beneviste, 2004). The amount of sterols is relatively constant among plant species 2–3 mg of total (free + sterified sterols) per dry gram plant. In fungi, the content of sterols is variable and may range from 0.005 to 2.9 wt/wt% depending on the species and habitat (Weete, 1973).

Sterols are steroid alcohols with an OH group on the first 6-C ring. The four hydrocarbon ring structure of steroids is made up of three 6-carbon rings and a 5-carbon ring. Sterols and steroids are synthesized via the acetate/mevalonate pathway of the isopropenoid metabolism. Isopentenyl diphosphate is the biological C_5 precursor of isoprenoids in plants (Lichtenhaler et al., 1997). Squalene synthase is the first enzyme of the sterol branch (Hartman, 2003). Key enzymes involved are 3-hydroxy-3-methyl glutaryl coenzyme A reductase or sterol-C-methyltransferase. The enzyme 3-hydroxy-3-methylglutaryl CoA reductase is a rate-limiting step for carbon flux toward sterols, and it positively or negatively responds to a depletion of endogenous sterols or accumulation of intermediates. Sterol methyltransferases and acyltransferase participate in sterol homeostasis. A coordinated regulation of the biosynthetic pathways of sterols and some specific lipids may occur during membrane biogenesis (Hartman, 2003). A minor proportion of sterols serve as precursors to steroid derivatives (Schaller, 2003).

Sterol biosynthesis in fungi produces ergosterol and other 24-methyl sterols (de Souza and Rodrigues, 2009). Ergosterol is the principal sterol in fungi (Hendrix, 1970). Fungi also contain cholesterol and stigmasterol,

and ergosterol may be a minor component in species of the Mucorales and *Saccharomyces cerevisiae* (Hendrix, 1970). In fungi, some parts of the sterol molecule are important for their activity in cellular membranes. The 3β-OH moiety is obligatory for growth, whereas the presence of methyl groups at C14 or C4 do not allow growth (de Souza and Rodrigues, 2009). Sterols can be decomposed by bacteria and other microorganisms as the sole source of carbon and energy (Buetal and Levedahl, 1964). A large number of sterols have antimicrobial effects on many bacteria, molds, yeasts, and protozoa (Kodicek and Worden, 1945).

Sterols help regulate the fluidity and permeability of phospholipid bilayers (Schaller, 2003). They are also involved in the embryonic development of vertebrates (Guy, 2000), and constituents of microdomains that serve as signaling centers for multiple pathways (Karpen et al., 2001). Sterols are precursors of brassinosteroids, hormones involved in plant growth and development, and sexual pheromones in fungi (Blunt and Silver, 1991). Steroids and sterols are responsible for the same outcomes in their metabolic functions. Steroids, however, do not participate in keeping the permeability and fluidity of the membrane nor do they participate in cell-signaling events. Excellent reviews on the biosynthesis, role, and regulation of plant sterols have been published by Beneviste (1986 and 2004), Schaller (2003), and Hartman (2003).

4.11. Esters of suberin in the soil solutions

4.11.1 Analysis by Py-FIMS of esters of suberin

Table 4.13 shows the identification of seven esters of suberin in the soil solutions. Their abundance was low at <2054 counts/μL, often in the hundreds of counts/μL. In spite of their low abundance, the maximum content of esters of suberin was observed at the flag stage of wheat growth, 53 days after seeding, and their contents decreased thereafter. Overall, the contents of suberin esters in soil solutions were the lowest of all chemical classes and their content in soil solution was very similar at the first and last stages of wheat growth.

4.11.2 Biochemistry and functions of suberin in rhizospheres

Suberin is a complex biopolymer found on the inner face of primary cell walls in aerial and root parts of the plant. Polyaliphatics and polyaromatics are the main molecular components (Bernards, 2002; Graça and Santos, 2007). The aliphatic domain is an insoluble polyester largely comprised of fatty acids and glycerol, such as ω-hydroxy fatty acids, α,ω-dicarboxylic acids, mid-chain

Table 4.13 Ion intensities (II) for *m/z* assigned to esters of suberin in soil solutions obtained from the rhizosphere at four different growth stages of wheat

	II (count × 10^2/μL) at wheat growth stage			
m/z	**IF031[a]**	**IF093[b]**	**IF137[c]**	**IF196[d]**
446	4.42	14.66	5.98	5.58
460	3.01	19.19	3.37	4.59
474	3.97	20.25	3.08	2.03
488	2.94	5.90	5.00	2.12
502	2.57	9.33	3.22	1.89
516	2.49	20.54	5.05	2.15
530	3.89	6.30	2.93	1.78
Total	23.29	91.67	28.63	20.14

[a]IF031 = four leaves unfolded (25 days after seeding).
[b]IF093 = flag leaf (53 days after seeding).
[c]IF137 = grain—early milk (72 days after seeding).
[d]IF196 = grain—dry seed (102 days after seeding).

oxygenated fatty acids, unsubstituted fatty acids, and primary fatty alcohols (Pollard et al., 2008). The phenylpropanoid-derived aromatic domain mostly consists of ferulate, which is a *p*-hydroxycinnamic acid (Bernards et al., 1995). Suberin is also rich in monomers ranging in size from C_{20} to C_{24}. The relative abundance of suberin monomer constituents varies considerably between species (Pollard et al., 2008). Another major component of the suberin aliphatic domain is glycerol (Moire et al., 1999), which in partial depolymerization experiments is found esterified to ω-hydroxy fatty acids and α,ω-dicarboxylic acids (Graça and Pereira, 2000).

Suberin helps control the movement of water, solutes, and gases between plants and soils or the environment.

5. SUMMARY OF COMPONENT CLASSES AND THEIR IIs

A summary of the 11 component classes and their IIs in soil solutions is presented in Table 4.14. Table 4.14 also shows the percentages of TIIs identified, which ranged from 69.5% at the flag leave stage to 83.1% at the grain hard seed stage, 102 days after seeding. An inspection of the yields (expressed as percentages of TIIs) identified in 11 classes shows that lipids (total fatty acids + alkanes + alkyl radicals) had the highest yield (25.2–33.6%), followed

Table 4.14 Summary of total ion intensities (TIIs) for *m/z* assigned to 11 chemical classes of compounds in soil solutions obtained from the rhizosphere at four different growth stages of wheat

	Total ion intensities at four wheat growth stages							
	IF031[a]		IF093[b]		IF137[c]		IF196[d]	
Chemical class	**Counts/μL**	**%**	**Counts/μL**	**%**	**Counts/μL**	**%**	**Counts/μL**	**%**
Carbohydrates	82,914	3.5	91,403	2.9	116,315	6.0	155,363	9.3
Amino acids	101,827	4.2	104,594	3.3	89,288	4.6	78,836	4.7
Lignin monomers[e]	146,736	5.3	168,599	6.1	140,113	7.2	171,398	10.2
Lignin dimers	163,271	6.8	213,990	6.8	67,011	3.5	59,905	3.6
Alkylbenzenes	71,454	3.0	101,181	3.2	71,104	3.7	69,534	4.1
Flavonoids	89,845	3.7	90,407	2.9	43,910	2.3	42,682	2.6
Alkyl radicals	233,197	9.7	151,133	4.8	103,446	5.3	70,853	4.2
Lipids[f]	574,513	23.9	668,879	21.1	386,749	19.9	379,141	22.6
N-compounds	393,545	16.6	532,867	17.0	398,375	20.8	356,245	21.5
Sterols[g]	15,835	0.7	69,194	2.2	14,558	0.8	9849	0.6
Esters of suberin	2329	0.1	9617	0.3	2863	0.2	2014	0.1
Subtotal assigned	1,875,466	78.1	2,201,864	69.6	1,433,732	73.9	1,395,820	83.3
TII (15–900 *m/z*)	2,400,905		3,163,439		1,941,295		1,676,096	
Volatile matter (%)	100		100		100		100	

[a]IF031 = four leaves unfolded (25 days after seeding).
[b]IF093 = flag leaf (53 days after seeding).
[c]IF137 = grain—early milk (72 days after seeding).
[d]IF196 = grain—dry seed (102 days after seeding).
[e]Lignin monomers and phenols.
[f]Lipids = total fatty acids + total alkanes.
[g]Sterols and steroids.

by N-components (16.6–21.5) and phenols and lignin monomers and dimers (10.7–13.8). The latter three classes, that is, lipids, N-components (mostly N-heterocyclics), and phenols + lignins, were the most abundant components in all soil solution samples. Next, in terms of concentrations, carbohydrates constituted 2.9–9.3%, amino acids 3.3–4.7%, alkylbenzenes 3.0–4.1%, flavonoids 2.3–3.7%, sterols and steroids 0.6–2.2%, and esters of suberins 0.1–0.3% of the compounds identified.

The data in Table 4.14 show that over the four wheat growth stages, the highest yields of most classes of compounds were obtained at the flag leaf stage, 53 days after wheat seeding. These yields were 17–58% higher than those found at the other three wheat growth stages. In turn, the TIIs for most classes of components were lowest at the grain hard seed growth stage, with a concentration 26% lower than that observed at the early four-leaf unfolded stage, 25 days after seeding wheat. The exceptions to these general observations were carbohydrates whose concentration in soil solution samples was highest at the hard grain growth stage. In addition, the highest concentration for unsaturated fatty acids with double bonds and for neutral amino acids was observed at the four-leaf stage, 25 days after seeding.

6. THE ROLE OF ROOT EXUDATES IN SOIL SOLUTIONS

Roots have played an essential role in the evolution of plants enabling them to meet the requirements of anchorage and the acquisition of water and nutrients, and are instrumental in the processes of soil pedogenesis and the cycling of minerals from soils to the biosphere (Kenrick, 2002). Roots, through their exudates, excrete a great diversity of organic compounds, thereby assisting the plant to control its surrounding environment, especially those processes regulating the interactions between plant and microbial communities in the rhizosphere. Root exudates are one of the ways for plants to chemically communicate with neighboring plants and microorganisms present in the rhizosphere. The chemical compounds of the root exudates are specific to a particular plant species and also depend on the nearby biotic and abiotic environment (Rovira, 1956).

To obtain an estimate of the amount of carbon exuded from wheat roots into the soil solutions throughout the growing season of wheat, amounts of soluble organic carbon in the solutions collected from planted soil pots were compared to those found in solutions of unplanted soil pots. Figure 4.6 presents the amounts of soluble organic carbon measured in the solution of planted and unplanted soil pots at the four wheat growth stages. The data

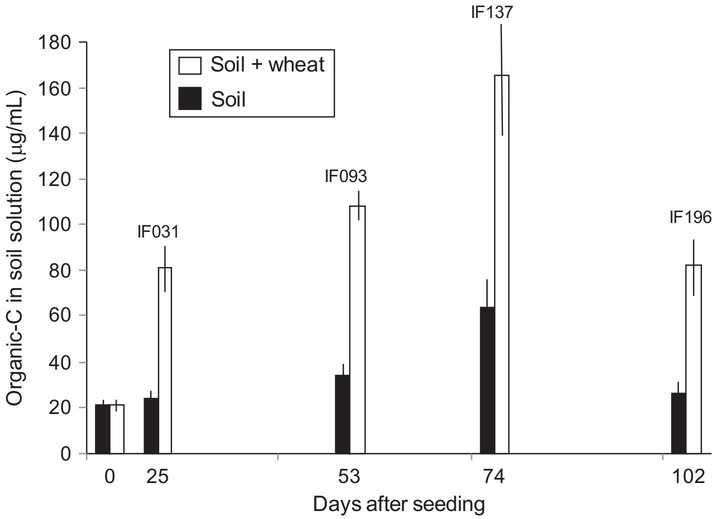


Figure 4.6 The content of soluble organic carbon in soil solutions collected at selected dates throughout the growing season from pots containing soil alone and soil + four wheat plants.

show that the presence of wheat plants increased the amount of soluble carbon in soil solutions relative to those amounts found in the unplanted soil during the growing season of wheat. These data show that the increased amounts of soluble carbon in the planted soil were associated to a large extent with the exudation of photosynthates by wheat roots. Contributions of soluble carbon in soil solutions are also expected from the release and decomposition of plant and microbial cells, but to a smaller extent. For example, the carbon content of the soil solution in planted soil increased 4 times after 25 days, 3 times after 53 days, 2.8 times after 74 days, and 3 times after 102 days after seeding. Parallel and complementary $^{13}CO_2$ labeling studies of the same soil pots planted to wheat confirmed that root exudation contributed to the soil solution with 16.5 mg ^{13}C/4 plants during 6 h of labeling at tillering. The concomitant amount of ^{13}C photosynthesized for the same labeling period by four plants was 24.1 mg (Monreal, unpublished data, 2012). These latter data show that root exudates add a significant amount of soluble organic carbon to the soil solution, an amount which was equivalent to 68% of the amount of CO_2-C taken up by wheat during one growth stage of wheat. Thus, it was important that we identified these organic components of soil solutions, as root exudates may help regulate the species composition of soil microbial communities and their activities during crop growth.

Root exudates consist of carbohydrates, amino acids, vitamins, organic acids, nucleotides, microbial stimulators and inhibitors, enzymes, aliphatic carboxylic acids, and several other compound classes (Dakora and Phillips, 2002). Rovira (1956) notes that plants differ considerably in both quantities and types of organic compounds they exude from their roots. VanCura and Hovadik (1965) report that root exudates from wheat and barley are similar in composition but significantly different from exudates from tomatoes and red peppers. According to Dakora and Phillips (2002), the chemical compounds in root exudates may act as regulators of microbial growth and functions, and involve molecules which directly control key microbial processes of nutrient cycling in the rhizosphere. In addition, plant roots have other functions in soil–plant systems including anchorage, provision of nutrients and water, and production of exudates with growth regulatory properties (Bertin et al., 2003). New evidence indicates that root exudates take part in signaling events that initiate the execution of complex biological interactions in soil–plant systems (Bais et al., 2006). The chemical compounds in root exudates act as regulators of microbial growth and function, and contain molecules which directly control the rhizosphere processes that enhance soil N mineralization and crop nutrient uptake and assimilation (Dakora and Phillips, 2002).

Barber and Gunn (1974) showed that 5.9% of the total plant weight was released as root exudates, while Barber and Martin (1976) reported that wheat and barley root exudates could comprise 7–13% of the total dry matter of plant grown axenically in soils and that nonsterile soil-root exudates accounted for 19–25% of the dry matter produced. Almost all root exudation studies have been conducted in hydroponic and axenic sand cultures in the absence of soil (Darwent et al., 2003; Rovira and McDougall, 1967). Substantial quantities of carbonaceous plant products enter the soil through root exudation, where they undergo a series of chemical and microbiological reactions about which little is known at this time (Schnitzer and Monreal, 2011).

Many components of root exudates are part of the pool of secondary metabolites synthesized by plants to defend themselves against nematodes, microbial pathogens, viruses, or competing plants; and also signal communications for interactions between plants and soil organisms to occur. For a long time, secondary metabolites were considered waste products of plant metabolism (Bennett, 1995). Nowadays, secondary metabolites are considered to have significant ecological functions which represent adaptive characters that have been subject to natural selection during evolution. This

requirement for secondary metabolites to have highly diverse biological activities has led plants to produce a vast catalog of compounds associated with their genome. Plant genomes are variously estimated to contain 20,000–60,000 genes, and perhaps 15–20% of these genes encode enzymes for secondary metabolism (Lattanzio et al., 2006). By comparison, the number of genes found in bacteria can range from a few hundred to <6000, and in fungi, this number may range from 6000 to 20,000 depending on the species.

7. SIMILARITIES IN CHEMICAL COMPOSITION OF SOIL SOLUTIONS AND SOIL HSs

A comparison of the compound classes identified in the four soil solutions and reported in this chapter shows great similarities with those of soil HSs such as humic acid, fulvic acid, and humin, analyzed by Py-FIMS in previous studies (Schnitzer, 2000; Schnitzer and Monreal, 2011; Schnitzer and Schulten, 1995). It has been hypothesized that root exudates provide the raw materials (i.e., simple oxoacids) for the synthesis of soil HSs via microbial PKTs and chemical reactions (Schnitzer and Monreal, 2011). Multiple ketonic CO groups of PKTs are also abundant in humic acid of a Mollisol, and in fulvic acid of a Haplaquod (Schnitzer and Schulten, 1998). These findings suggest that HSs are synthesized by chemical and microbiological reactions, from compounds in soil solutions originating mainly from root exudates. The soil solution is a complex but favorable medium for both chemical and microbiological syntheses and other reactions due to its relative high content of carbon, nitrogen, water, and many organic and inorganic nutrients (Monreal and McGill, 1989a).

8. PROPOSED MECHANISMS OF HS SYNTHESIS

In this chapter, we hypothesize, further, that during the growing season, the increased thermal stability of organic compounds in soil solutions at the hard grain growth stage of wheat reflects, among other, the potential biotic and abiotic synthesis of soil HS such as humic acid, fulvic acid, and humin. The soil solution, at the interface with inorganic colloids and the soil atmosphere, offers a very favorable site for complex biotic and abiotic interactions. The microbial synthesis of PKTs by multiple polyketide synthases in nature and soils involves condensation, chain elongation, and cross-linking reactions followed by catalysis of PKTs by clay colloidal

surfaces (Schnitzer and Monreal, 2011). Further research is warranted to continue testing the hypothesis of HS synthesis from soil solution compounds via PKTs.

9. SIGNIFICANCE OF THE ORGANIC COMPONENTS RESIDING IN SOIL SOLUTIONS FOR AGRI-ECOSYSTEMS

Chemical, microbial, and biochemical information on the composition of soil organic matter in soil solutions is important from agronomic, economic, environmental, and social viewpoints. For example, molecular information of the composition of soil solutions allows to shed light on binding mechanisms between organic molecules with metals, xenobiotics, and other contaminants and/or agrochemicals (Simpson et al., 2011). The latter information is vital to assess health risks to humans and wildlife associated with the transport and persistence of man-made and naturally synthesized nanoparticles in soils, sediments, water, and the atmosphere. In addition, detailed information on the chemical composition of organic compounds in soil solutions will enable accurate assessments of the energy and nutrient flows in native and disturbed soil–plant ecosystems. Soil solutions are chemical and biochemical mirrors where we can tell the interactions between plants and microorganisms (i.e., antagonistic, pathogenic, and beneficial symbiotic and mycorrhizal colonizing). The organic composition of the soil solution composition allows us to explain and model the microbial and biochemical mechanisms of response of biological systems to different perturbations in agro-ecosystems. Knowing the chemical composition of soil solutions is a prerequisite to understanding the interactions between root exudation and microbial processes controlling nutrient mineralization in synchrony with the uptake of nutrients by agronomic crops. A better knowledge of the chemical composition of the soil solution will allow us to explain and model the mechanisms of response of biological systems to different anthropogenic perturbations and environmental stresses in agro-ecosystems.

In particular, new knowledge on the molecular composition of organic constituents in soil solutions is key for (a) understanding the sources and amounts of organic N-, P-, and S-containing compounds that help maintain soil fertility and other ecological functions; (b) understanding the interactions between root exudates and soil microorganisms to effect the mineralization processes of soil organic N, P, and S; (c) understanding the environmental and human health risks of contaminants; (d) establishing mass

spectrometric databases of soil metabolomic studies to help describe the responses of living systems to disease, genetic, anthropogenic, and environmental disturbances, and biological interactions in soil–plant environments (Dettmer et al., 2007); (e) understanding the metabolism and function of secondary metabolites (i.e., polyketides, flavonoids, alkaloids) produced by plants and soil microorganisms within rhizospheres; (f) testing/elucidating the role of simple organic compounds in the synthesis of soil PKTs for HS formation (Schnitzer and Monreal, 2011); (g) designing environmentally sound, cost-effective chemical and biological remediation strategies for soils; (h) increasing knowledge of biogeochemical processes and components; (i) establishing the mechanisms of interactions of natural and man-made nanoparticles with soluble organics and metals and their transport and stabilization through soil, water, and sediments; (j) determining the effects of crop type and growth stage on the chemical composition of organic compounds in soil solutions and its effect on soil microbial metabolism and community composition; and (k) evaluating the effects of the five soil-forming factors (i.e., topography, drainage, climate, vegetation, and soil parent materials) on the chemistry and dynamics of soil organic matter pools with different turnover times.

10. CONCLUSIONS

The organic components in soil solutions of wheat rhizosphere were characterized by Py-FIMS at four different growth stages. We identified 346 organic components which were grouped into 11 chemical classes: carbohydrates, amino acids, phenols + lignin monomers, lignin dimers, flavonoids, alkyl radicals, fatty acids + alkanes, N-heterocyclics, other N-compounds, sterols and steroids, and esters of suberin. The highest content of classes of components and individual chemical species in soil solutions were lipids, N-heterocyclics, and phenols + lignin monomers and dimers. Their highest content occurred at the flag leaf growth stage, except for carbohydrates, whose content in solution was highest at the hard grain growth stage. Organic components in soil solutions originate mostly through crop root exudation and by microbial metabolism; however, the biosynthetic pathways for many of these compounds are still unknown. Some of the identified compounds are associated with chemical signaling interactions between plants and soil microorganisms, and are also used as C, N, and energy sources by soil heterotrophs. Many organic components of soil solutions are secondary plant metabolites which represent key weapons in the

continuous competition, synergy and struggle of plant and soil microorganisms for ensuring vital space, and access to carbon, nitrogen, and other nutrients and energy resources in terrestrial ecosystems. As characterized by Py-FIMS, the chemical components of the four soil solutions from wheat rhizosphere resembled that of HSs. The latter suggests that soil solutions constitute a favorable medium that continuously receive and provide the organic substrates necessary for soil life and the synthesis of complex HSs.

ACKNOWLEDGMENTS

The authors thank the Alberta Innovates Bio Solutions and Agriculture and Agri-Food Canada for funding. The authors also thank S. Orozovic, T. Wu, F. Matus, B. Mah, S.S. Wu, and P. Etcheverria for their support in greenhouse studies conducted to better understand the dynamics of organic compounds in root exudates from wheat during the growing season. We also thank P. Leinweber for the Py-FIMS analysis of soil solution samples.

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CHAPTER FIVE

Sustainable Management of Soils of Dryland Ecosystems of India for Enhancing Agronomic Productivity and Sequestering Carbon

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Contents

Advances in Agronomy, Volume 121
ISSN 0065-2113
http://dx.doi.org/10.1016/B978-0-12-407685-3.00005-0

Abstract

Soil organic carbon (SOC) is a strong determinant of soil quality and crop productivity, especially in the arid and semiarid environments of the tropics. Drought stress, high temperatures reaching up to 45 °C for 8–10 weeks in a year, coupled with low biomass productivity are common features of dry agroecosystems. India, with only 2.5% of the world's geographical area, is a home to 17% of the global population. Population increased from 361 million in 1951 to 1140 million in 2011, more than threefold increase over 50 years. Productivity levels of rainfed dryland crops are far below those of global average. Thus, increasing productivity of rainfed cropping systems is an urgent task to meet the food demand of an ever-increasing population because 57% of the total arable land area of 141 Mha is under rainfed farming.

Yields of important rainfed production systems in long-term manurial experiments under different climate and soil types show declining trends even with adoption of some recommended management practices (RMPs). Some RMPs include diverse crop rotations with legumes, and integrated nutrient management (INM) involving addition of farmyard manure (FYM), use of groundnut shells (GNS) and other crop residues (CRs), green leaf manuring (GLM), etc. These RMPs have been tested in seven long-term experiments of 13–27 years duration established in diverse soils and agroecoregions.

These studies, under the auspices of the All India Coordinated Research Project on Dryland Agriculture (AICRPDA), were conducted under diverse soil and climatic conditions, viz., Anantapur and Bengaluru (Alfisol), Solapur and Indore (Vertisol), Sardar Krushinagar (Entisol), and Varanasi (Inceptisol). Seven rainfed cropping system experiments involved major crops of the region including groundnut (*Arachis hypogaea*), finger millet (*Eleusine coracana*), winter sorghum (*Sorghum bicolor*), pearl millet (*Pennisetum glaucum*), cluster bean (*Cyamopsis tetragonoloba*), castor (*Ricinus communis*), soybean (*Glycine max*), safflower (*Carthamus tinctorius*), lentil (*Lens esculenta*), and

upland rice (*Oryza sativa*). Diverse nutrient management treatments assessed included cattle manure, green leaf manure, crop residues, and chemical fertilizers. Common soil fertility management treatments across seven experiments were control (no fertilizer or organics), 100% recommended dose of fertilizers (RDFs), 50% RDF + 50% organics, and 100% organics.

Maintaining or improving SOC concentration in rainfed dryland agroecosystems is a major agronomic challenge. Yet, the data from long-term experiments show that increasing SOC concentration by C sequestration and stabilization positively affects yields of several crops. Agronomic efficiency of added nutrients and partial factor productivity of crops are maintained or enhanced with INM practices including application of organics in conjunction with chemical fertilizers, but decline with application of only chemical fertilizers because of declining SOC concentration and soil quality with continuous cropping. In comparison with the control, grain yield of all crops are increased significantly with the adoption of INM practices using locally available organic resources.

The magnitude of increase in yield (Mg ha^{-1}) in respect to control is from: (1)0.78 to 1.03 in groundnut with 50% RDF + FYM 4 Mg ha^{-1}, (2) 0.40 to 1.34 and 0.82 to 3.96 in groundnut and finger millet, respectively, through FYM 10 Mg ha^{-1} + 100% NPK in groundnut–finger millet rotation, (3) 0.84 to 3.28 in finger millet through FYM 10 Mg ha^{-1}+100% NPK, (4) 0.61 to 1.19 in winter sorghum through 25 kg N ha^{-1} (*Leucaena* clippings) + 25 kg N ha^{-1} (urea), (5) 0.43 to 0.81, 0.32 to 0.58 and 0.44 to 0.83 in pear millet, cluster bean, and castor, respectively, through 50% RDN (fertilizer) + 50% RDN (FYM), (6) 1.04 to 2.10 and 0.63 to 1.49 in soybean and safflower, respectively, through FYM 6 Mg ha^{-1} + 20 kg N + 13 kg P ha^{-1}, and (7) 1.08 to 1.95 and 0.48 to 1.04 in rice and lentil, respectively, through 50% N (FYM) + 50% RDF treatment.

Treatments receiving INM practices also exhibited higher sustainable yield index (SYI) over unfertilized control and sole application of either chemical fertilizers or organic manures. For every Mg ha^{-1} increase in SOC stock in the root zone, there was an increase in grain yield (kg ha^{-1}) of 13 for groundnut, 101 for finger millet, 90 for sorghum, 170 for pearl millet, 145 for soybean, 18 for lentil, and 160 for rice.

Improved nutrient management practices were identified on the basis of the mean rate of SOC sequestration. The average SOC sequestration rate (kg C ha^{-1}year^{-1}) measured with different management treatments were: (1) 570 for 50% RDF + 4 Mg ha^{-1} GNS, (2) 570–720 for FYM 10 Mg ha^{-1} + 100% NPK, (3) 650 for 25 kg N ha^{-1} (sorghum residue) + 25 kg N (*Leucaena* clippings), (4) 240 for 50% RDN (fertilizer) + 50% RDN (FYM), (5) 790 for FYM 6 Mg ha^{-1} + 20 kg N + 13 kg P, and (6) 320 for 100% organic (FYM). The critical level of C input requirements for maintaining SOC at the antecedent level ranged from 1 to 3.5 Mg C ha^{-1} year^{-1} and differed among soil type and production system. The critical level of C input was higher in soybean system and lower in winter sorghum system and increased with increase in mean annual temperature from humid to semiarid to arid ecosystems.

Thus, RMPs based on locally available organic resources are a win–win situation for improving productivity and SOC sequestration, thus advancing food security and improving the environment.

1. INTRODUCTION

The global rainfed cropland area is estimated at 1.132 billion ha at the end of the last millennium (Biradar et al., 2009), which is 2.78 times the gross irrigated area (407 million ha or Mha) of the world (http://www.iwmigiam.org/info/main/aboutGMRCA2.asp). Rainfed agroecosystems occupy a considerable place in Indian agriculture too, covering 80 Mha, in arid, semi-arid, and subhumid climatic zones, constituting nearly 57% of the net cultivated area. India has 17% of world's population and 15% of the world livestock but has only 2.5% of the geographical area, 4.2% of fresh water resources, 1% of forests, and 0.5% of pasture land (Srinivasarao, 2011). Rainfed area in India contributes almost 100% of forest products, 84–87% of coarse grain cereals and pulses, 80% of horticulture, 77% of oilseeds, 60% of cotton (*Gossypium hirsutum*), and 50% of fine cereals including rice (*Oryza sativa*), wheat (*Triticum aestivum*), maize (*Zea mays*), sorghum (*Sorghum bicolor*), etc. (Srinivasarao et al., 2010, 2011a). Rainfed regions support 60% of livestock and 40% of human population and contribute 40% of food grains and several special-attribute commodities such as seed spices, dyes, herbs, gums, etc. (Srinivasarao, 2011). However, double-cropped area in rainfed farming is negligible. Rainfed agroecoregions are complex, diverse, fragile, risky, underinvested, and require regionally differentiated investments and management strategies. Drought stress, in conjunction with high temperatures reaching up to 45 °C for 8–10 weeks in a year, coupled with low biomass productivity are common features of dry agroecosystems. Achieving high agronomic production is difficult in these rainfed areas due to vagaries of rainfall and degraded soils.

The above-mentioned statistics indicate the high pressure on finite natural resources. The net sown area in India has remained constant for many years at 141 Mha, but the human and livestock population has been steadily increasing. The slowdown in agricultural productivity growth has been attributed to resource degradation problems and declining factor productivity in major production systems. With the skewed and intense rainfall and concurrent rise in temperatures, the fertile top soil is prone to degradation. Low factor productivity in Indian agriculture has raised serious concerns in terms of economy as well as environmental quality. Progressively more and more inputs are needed for unit production of food. The depletion of soil organic matter (SOM) is responsible for a declining response to fertilizers and widespread deficiencies of secondary and micronutrients. Therefore,

improving SOM concentration may be an important option. The objective of this chapter is to describe several relevant issues regarding sustainable management of dryland soils to enhance agronomic productivity and promote soil C sequestration.

2. FEATURES OF DRYLAND ECOSYSTEMS

Arid and semiarid regions comprise almost 40% of the world's land area and are inhabited by some 2 billion people (ICRISAT, 2010). Approximately 60% of these drylands are in developing countries, where grain yields average about half of those in irrigated areas (1.5 vs. 3.1 Mg ha^{-1}). The current lack of governance, management, and investment priorities given to upgrading rainfed agriculture in developing countries are often justified by the "marginal" potential in rainfed areas and the major water scarcity problems in "dryland" areas (Rockström, 2010). In India, about 114 km^3 of runoff is generated from 28 Mha of rainfed area in central and eastern India alone (Venkateswarlu and Prasad, 2012). A major adverse feature of rainfed areas is the long spells of drought followed by heavy rains causing floods. In a normal year, about 25 Mha of rainfed area can be provided with one supplemental irrigation (10 cm), with an estimated harvestable surplus of 28 km^3. In a drought year, the area that can be irrigated once is about 20 Mha.

2.1. Climate

Climate of rainfed–dryland areas varies from arid, semiarid to subhumid, with mean annual rainfall ranging from 412 to 1378 mm (Table 5.1). Soils are Inceptisols, Alfisols, Vertisols/Vertic subgroup, and Aridisols/Entisols (desert type). Length of the growing period ranges from 60–90 days in the arid regions to 180–210 days in the subhumid regions. The Planning Commission of India (1989) divided the country into 15 agroclimatic zones, but the National Agricultural Research Project (NARP) identified 127 agroecological zones (Ghosh, 1991). Further, the National Bureau of Soil Survey & Land Use Planning (NBSSLUP, 2004) has divided the country into 20 homogenous agroecological regions and 60 subregions based on topography, climate, soils, and effective growing seasons (Sehgal et al., 1990). In view of the variability of the crop-growing conditions under semiarid and subhumid conditions, the climatic zones have been regrouped by the Central Research Institute for Dryland Agriculture (CRIDA, 2008) in relation to rainfall, length of growing period, and agro ecological subregion

Table 5.1 Soil type, climate, rainfall, and rainfed production systems in India

Location/state/ production system	Climate	Soil type	Mean annual rainfall (mm)	Growing period (days)
1. Varanasi, U.P. (rice)	Subhumid	Alluvial-deep Inceptisols	1080	150–180
2. Faizabad, U.P. (rice)	Subhumid	Alluvial-deep Inceptisols	1057	150–180
3. Agra, U.P. (pearl millet)	Semiarid	Alluvial-deep Inceptisols	665	90–120
4. Ballowal Saunkri, Punjab (maize)	Semiarid	Alluvial-deep Inceptisols	1000	120–150
5. Rakh Dhiansar, J&K (maize)	Semiarid	Alluvial-deep Inceptisols	1180	150–210
6. Jhansi, U.P. (Rabi-Sorghum)	Semiarid	Alluvial-deep Inceptisols	1017	120
7. Phulbani, Orissa (rice)	Subhumid	Red/yellow deep Alfisols	1378	180–210
8. Ranchi, Jharkhand (rice)	Subhumid	Red-shallow Alfisols	1299	150–180
9. Anantapur, A.P. (groundnut)	Arid	Red-shallow Alfisols	590	90–120
10. Bengaluru, Karnataka (finger millet)	Semiarid	Red-deep Alfisols	926	120–150
11. Rajkot, Gujarat (groundnut)	Arid	Black-deep Vertisols	615	60–90
12. Indore, M.P. (soybean)	Semiarid	Black-deep Vertisols	944	120
13. Rewa, M.P. (soybean)	Subhumid	Black-medium deep Vertisols	590	150
14. Akola, Maharashtra (cotton)	Semiarid	Black-medium deep Vertic/ Vertisols	825	120–150
15. Kovilpatti, Tamil Nadu (cotton)	Semiarid	Black-deep Vertisols	743	120
16. Bellary, Karnataka (rabi sorghum)	Semiarid	Black-deep Vertisols	500	90–120

Table 5.1 Soil type, climate, rainfall, and rainfed production systems in India—cont'd

Location/state/ production system	Climate	Soil type	Mean annual rainfall (mm)	Growing period (days)
17. Bijapur, Karnataka (rabi sorghum)	Semiarid	Black-medium deep Vertisols	680	90–120
18. Solapur, Maharashtra (rabi sorghum)	Semiarid	Black-medium deep Vertic/ Vertisols	723	90–120
19. Arjia, Rajasthan (maize)	Semiarid	Black-shallow deep Vertisols	656	90–120
20. Hisar, Haryana (pearl millet)	Arid	Alluvial-deep Aridisols	412	60–90
21. Sardar Krushinagar, Gujarat (pearl millet)	Arid	Desert-deep Aridisols	550	60–90

Source: Srinivasarao et al. (2009a) and Srinivasarao and Vittal (2007)

(Table 5.2). This classification characterizes the suitability and potential of each subregion for a given land use and cropping/farming system.

2.2. Trends in key weather parameters

Rainfall, amount and distribution, is the key variable influencing crop productivity in rainfed farming. Intermittent and prolonged droughts are among major causes of yield reduction in most crops. Long-term data for India indicate that rainfed areas experience 3–4 drought years in every 10-year period. Of these, two to three are in moderate and one or two may be of severe intensity. However, so far no definite trend has been identified as a specific climate change fingerprint. For implementing any policy initiatives relevant to research and development (R&D), it is important to know the spatial distribution of drought events in the country. A long-term analysis of rainfall trends in India (1901–2004) using Mann Kendall test of significance by CRIDA indicates significant increase in rainfall trends in West Bengal, Central India, coastal regions, south western Andhra Pradesh, and central Tamil Nadu (AICRPAM, 2009–2010; Fig. 5.1). In contrast, a significant decreasing trend was observed in central part of Jammu & Kashmir, Northern MP, central and western part of UP, and northern and central part of Chhattisgarh. Analysis of the number of rainy days based on the India Meteorological Department (IMD) grid data from 1957 to 2007 shows declining trends in Chhattisgarh, Madhya Pradesh, and Jammu &

Table 5.2 Regrouping of agroecological subregions of the country based on climate types

Type of climate	Annual rainfall (mm)	Moisture index I_m (%)	Growing period (days)	Agroecoregion/subregion	Physiography	Area (Mha)
Cold arid	<500	>−66.7	60–90	1.1, 1.2	Western Himalayas, parts of J & K	14.31
Hot arid	<500	>−66.7	<90	2.1, 2.2, 2.3, 2.4, 3.0	Western plains and Kutch Peninsula, Deccan plateau	38.08
Semiarid						
Dry	500–700	−66.7 to −55.8	90–120	4.1, 4.2, 5.1, 6.1, 7.1, 8.1, 14.1, 18.1	Northern plains, Central highlands including Aravallis. Deccan plateau, Tamil Nadu uplands, South Tamil Nadu plains	41.57
Moist	750–1000	−55.7 to −33.3	90–50	4.3, 4.4, 5.2, 5.3, 6.2, 6.3, 7.2, 8.2, 8.3, 9.1, 18.2	Indo-Gangetic plains, Bundelkhand uplands, Malwa plateau, eastern Gujarat plain, Vindhyan hills, Central and western Maharashtra, North Karnataka, Vidarbha, North Telangana, Central Karnataka, Tamil Nadu plains, Punjab, and Rohilkhand	72.15
Subhumid						
Dry	1000–1200	−33.3 to 0.0	150–180	6.4, 7.3, 9.2, 10.1, 10.2, 10.3, 11.0, 12.3,14.2, 18.3	Western Karnataka plateau, eastern Ghats (south), South Bihar plains, Rohilkhand, Malwa plateau, Vindhyan Scariland, Narmada valley, Bundelkhand plateau, Chhattisgarh, Mahanadi basin, Chotanagar plateau, Gujarat hills, South Kashmir, and Andhra plain	57.99

Moist	1200–1600	0.0–20.0	150–210	10.4, 12.1, 12.2, 13.1, 13.2, 18.4	Satpura range and Wainganga valley, Gujarat hills, eastern Ghats, North Bihar, Fort hills of Central Himalayas, Utkal plains, and East Godavari Delta.	35.85
Humid and per-humid						
Humid	1600–2000	20.0–1000.0	180–270	15.2, 18.5, 19.1, 19.2, 19.3, 20.2	Parts of western and eastern Himalayas, Bengal basin, and Assam plains	33.3
Per-humid	>2000	>100	>270	14.3, 14.4, 14.5, 15.3, 15.4, 16.1, 16.2, 16.3, 17.1, 17.2, 20.1	Parts of eastern Himalayas, northeastern hills, western Ghats, and coastal plains	31.3

Compiled by CRIDA (AICRPAM) using NBSS and LUP data.

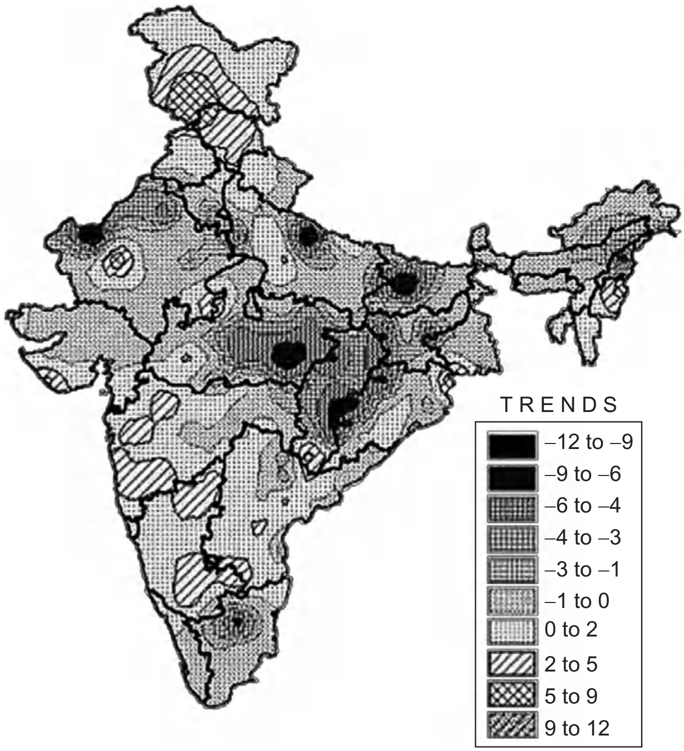

Figure 5.1 Rainfall trends over India from 1901 to 2004 (AICRPAM (2009–2010)).

Kashmir. In Chhattisgarh and eastern Madhya Pradesh, both rainfall and number of rainy days are declining, which is a cause of concern as this is a rainfed rice production system supporting large resource-poor tribal population with low adaptation capabilities. Mean temperature trends at 47 locations in India indicate an increasing temperature at several locations and either constant or a decreasing trend at others (Fig. 5.2).

3. SOILS OF DRYLANDS

India's diverse soil types can be grouped into eight orders. Taxonomically, soils of India fall under Entisols (80.1 Mha), Inceptisols (95.8 Mha), Vertisols (26.3 Mha), Aridisols (14.6 Mha), Mollisols (8.0 Mha), Ultisols (0.8 Mha), Alfisols (79.7 Mha), Oxisols (0.3 Mha), and miscellaneous types (23.1 Mha). In terms of the distribution of rainfall, 15 Mha of the land receives annual rainfall of <500 mm, 15 Mha of 500–750 mm, 42 Mha of 750–1150 mm, and 25 Mha of >1150 mm. In terms of land use and

Figure 5.2 Long-term (>50 years) mean annual temperature (°C) trends at 47 locations in India. *Source: Rao et al. (2010).*

management, alluvial (Inceptisols) soils are the most dominant (93.1 Mha) followed by red (Alfisols) soils (79.7 Mha), black (Vertisols) soils (55.1 Mha), desert (Entisols, Aridisols) soils (26.2 Mha), and lateritic (Plinthic horizon) soils (17.9 Mha; Table 5.3). In context of the ecosystem and regulatory services (provisional and regulatory services comprising production of biomass and forestry products, buffering action) and the economic goods (food, feed, fuel, and fiber production), these soils are crucial in terms of the crop and livestock production systems in India and are highly integrated into a farming systems mode.

4. PRODUCTIVITY OF DRYLAND CROPS

Soil characteristics and climatic factors listed above are among major constraints to achieving high productivity levels of rainfed crops grown by resource-poor farmers. Thus, the yield gaps between potential, on-station

Table 5.3 Major soil groups and their moisture storage capacities in rain-dependent areas of India (Srinivasarao, 2011)

Broad soil group	Subgroup (based on soil depth)	Moisture storage capacity (mm)
Vertisols and related soils	Shallow to medium (up to 45 cm)	135–145/45 cm
	Medium to deep (45–90 cm)	145–270/90 cm
	Deep (>90 cm)	300/m
Alfisols and related soils	Shallow to medium (up to 45 cm)	40–70/45 cm (sandy loam)
	Deep (>90 cm)	70–100/45 cm (loam)
		180–200/90 cm
Aridisols	Medium to deep (up to 90 cm)	80–90/90 cm
Inceptisols	Deep	90–100/m (loamy sand)
		110–140/m (sandy loam)
		140–180/m (sandy loam)
Entisols	Deep	110–140/m (sandy loam)
		140–180/m (loam)

and farm yields, and adopted crop management practices are high (Srinivasarao et al., 2010). Unless better water and nutrient management technologies are adopted, along with improved seed combination, harnessing the benefits of modern technologies to enhancing crop production cannot be realized.

The large yield gap between demonstration plots managed by scientists and actual national averages exist in most cereals as well as oilseed crops. Agronomic yield directly or indirectly is the determinant of the nutrient use efficiency (NUE) of the crop, and of the soil and agronomic factors that increase crop yield and improve the NUE. Prior to any discussion on management factors, it is appropriate to assess the potential and attainable yields of crops in different regions of India. Some examples of data on potential yield, on-station yield, and on-farm yield for the regions where research stations are located are presented in Fig. 5.3.

There exists a yield gap of 37–52% between potential and on-station yields, and 35–70% between potential and on-farm yields. The gap between on-station and on-farm yields ranges between 6% and 44%. In general, the yield gaps are wider in rice than wheat. The adoption of recommended

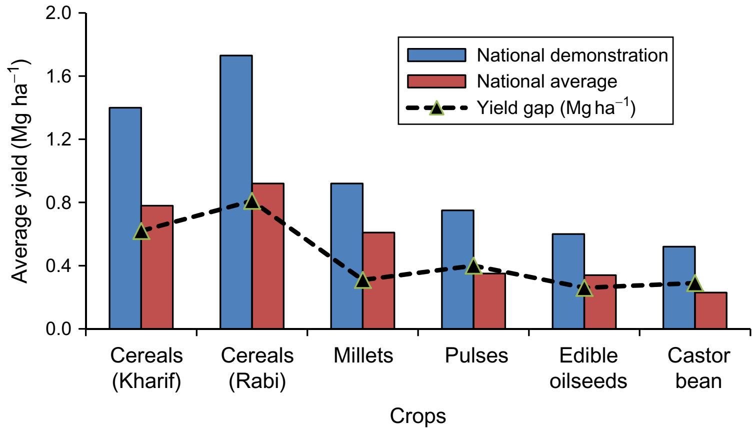

Figure 5.3 Yield gaps in dryland agriculture in India (Srinivasarao, 2011).

management practices (RMPs) can reduce the on-station versus on-farm yield gap, which can increase rice and wheat production by 15–20%. The fact remains that the yield gap between on-station versus on-farm is zero in Ludhiana region of Punjab for rice, and in Pantnagar, Uttaranchal for wheat. These trends show that farmers have already adopted RMPs in these regions. Thus, with good extension programs, the yield gap can also be abridged in other regions of the country. Information on benefits of adopting RMPs vis-à-vis the farmers' practices in increasing crop yield is also available for oilseeds (Hegde and Babu, 2008) and pulses (Ali et al., 2002).

Rainfed crops are largely grown on marginal and submarginal lands and receive least attention of farmers toward application of fertilizers and manures. Thus, nutrient deficiencies are emerging as the most important constraints to achieving the yield targets in these crops. In most of the rainfed crops, for example, in pulses (food legumes; Fig. 5.4), average on-farm yields are about one third of the potential yields on research plots and half of the yield in on-farm demonstration plots. Therefore, the rainfed agriculture in India has a vast but an untapped potential. Adoption of RMPs, synchronizing nutrient application with moisture availability or rainfall and timely weed control can improve crop yields (Table 5.4).

4.1. Long-term productivity trends

4.1.1 Groundnut

Groundnut (*Arachis hypogaea*) is one of the most important oilseed crops in India. But its average productivity is extremely low under rainfed conditions, and is about 1 Mg ha^{-1}. Long-term yield analysis shows negative slope

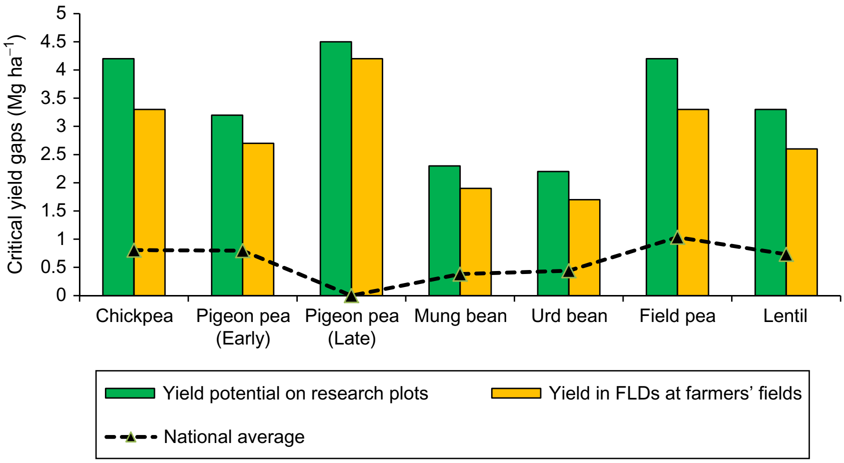

Figure 5.4 Critical yield gaps (Mg ha^{-1}) in major rainfed pulse crops (Chaturvedi and Ali, 2002).

with decreasing trends over time, which is a major concern (Fig. 5.5A). Groundnut is mostly grown on low fertility soils of marginal rainfed areas.

4.1.2 Finger millet

Finger millet (*Eleusine coracana* (L.) Gaertn) is the most important small millet in the tropics (12% of global millet area), and is cultivated in more than 25 countries in Africa and Asia, predominantly as a staple food grain. Finger millet has high yield potential (>10 Mg ha^{-1} under optimum irrigated conditions). In India, it is cultivated on 1.8 M ha, with average yields of 1.3 Mg ha^{-1} (FAO, 2009). Major finger millet growing area is confined to the southern parts of India. Positive trend of yield is observed with the application of organics along with mineral fertilizers (Fig. 5.5B).

4.1.3 Finger millet–groundnut rotation

The finger millet–groundnut rotation is common in semiarid belt of southern India. It supposedly improves soil fertility and productivity. Groundnut monocrops usually run for 2–3 years. Otherwise, groundnut is rotated with cereals like finger millet, sorghum, pearl millet (*Pennisetum glaucum*), and other millets, rice and maize or with other crops like pulses, sunflower (*Helianthus annuus*), and safflower (*Carthamus tinctorius*). Negative yield trend over time is observed in cereal–legume rotation also (Fig. 5.6A and B).

Table 5.4 Average yield of crops under improved versus common practices

Region	Crop	Mean yield (Mg ha^{-1})	
		Common practices	Improved practices
Agra	Pearl millet	0.79	1.72 (117.7)
	Mustard	0.85	1.58 (85.9)
	Barley	1.1	1.89 (71.8)
Anand	Pearl millet	2.45	3.29 (34.3)
	Tobacco	0.52	0.73 (40.4)
Anantapur	Groundnut	0.96	1.71 (78.1)
Dehra Dun	Maize	0.92	2.91 (216.3)
	Wheat	1.01	2.35 (132.7)
Hyderabad	Sorghum	1.23	2.89 (135.0)
	Castor	1.09	1.84 (68.8)
Kovilpatti	Sorghum	0.18	1.31 (627.8)
Ludhiana	Maize	1.85	2.97 (60.5)
	Wheat	1.56	3.07 (96.8)
Ranchi	Upland rice	1.40	3.11 (122.1)
	Barley	0.45	1.59 (253.3)
Solapur	Sorghum	0.53	2.48 (367.9)
	Safflower	0.88	1.56 (77.3)
Varanasi	Barley	0.76	1.39 (82.9)

Source: Reports of the respective Dryland Research Centres (AICRPDA)

4.1.4 Rice–lentil

Rice-based cropping systems are the backbone of India's food security, covering a total area of 38 Mha (FAI, 2010). Low yielding traditional varieties, low soil fertility, and soils depleted of soil organic carbon (SOC) stocks are among major constraints to increasing and stabilizing the productivity of rainfed rice. Lentil (*Lens esculenta*) is also adapted to local harsh climate and low fertility soil conditions. Because of its adaptation to intercropping and relay cropping, lentil occupies a unique place in cropping systems in northern, eastern, and central India. It is seeded into a standing paddy crop just before the harvest. Its incorporation into the rice-based cropping system improves SOC

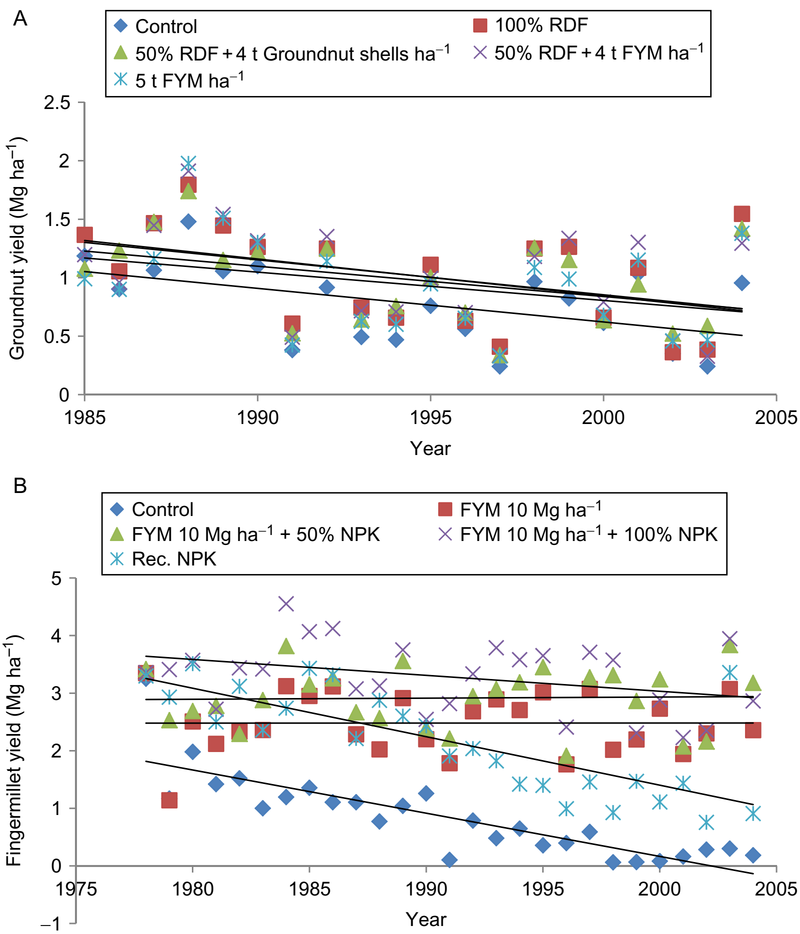

Figure 5.5 Time series yield trends of rainfed (A) groundnut during 20 years and (B) finger millet during 27 years with different nutrient management options in Alfisols of SAT India.

concentration by increasing crop residue (CR) inputs, recycling, and integrating use of organics along with mineral fertilizers, and sustaining productivity of upland rice-based systems. In rice and lentil-based systems, there is a positive yield trend particularly with better nutrient management (Fig. 5.7A and B).

4.1.5 Winter sorghum

Sorghum is an important cereal grown in the post monsoon season in south-central India. Resource-poor and small-size land holders depend on the productivity and sustainability of sorghum. Inclusion of CR/FYM/green leaf

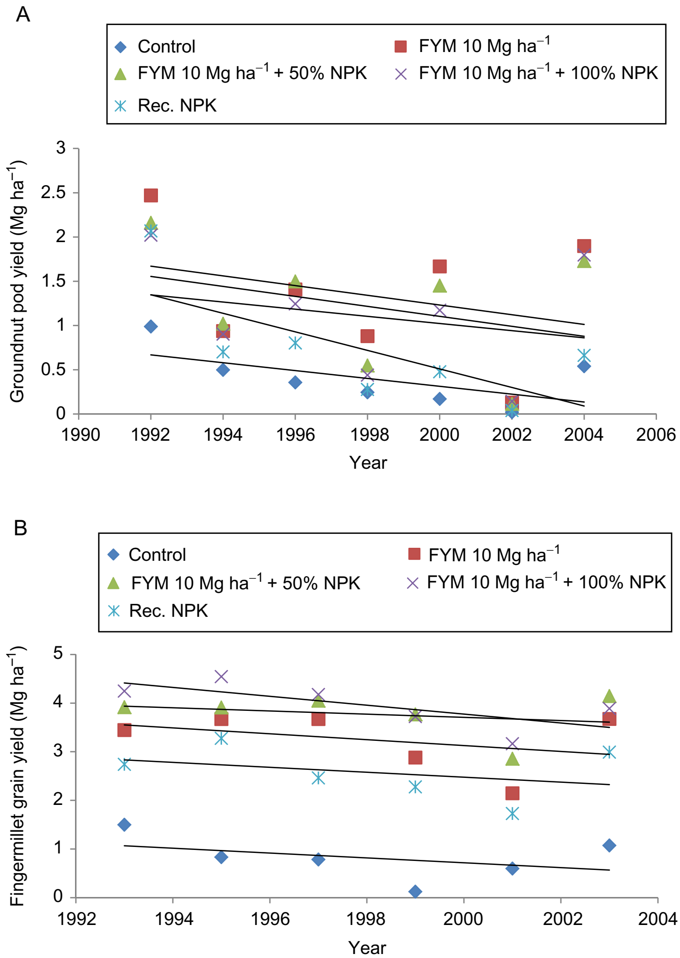

Figure 5.6 Time series yield trends of rainfed (A) groundnut (B) finger millet under groundnut–finger millet rotation during 13 years with different nutrient management options in Alfisols of SAT India.

manuring as integrated nutrient management (INM) leads to positive slope in long-term yield trend (Fig. 5.8).

4.1.6 Soybean

Soybean (*Glycine max*), designated as "golden bean," has established its potential as an industrially vital and a viable oilseed crop in India. Soybean is grown extensively in Madhya Pradesh, Maharashtra, and Rajasthan, and in some parts of Karnataka, Uttar Pradesh, Tamil Nadu, and Andhra Pradesh as a

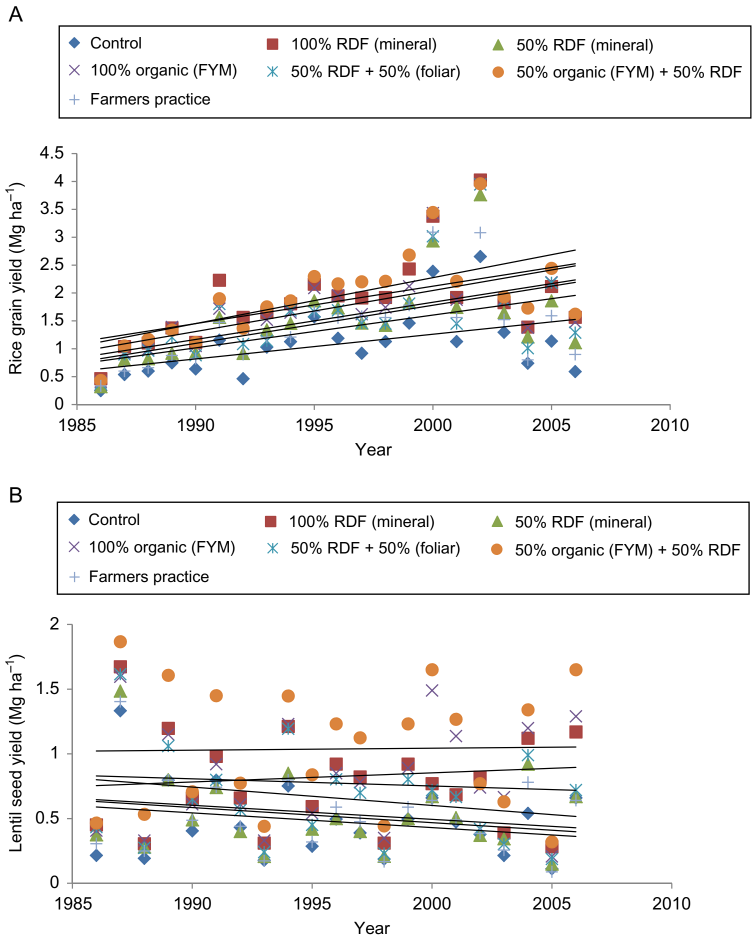

Figure 5.7 Time series yield trends of rainfed (A) rice and (B) lentil under rice–lentil sequence during 21 years with different nutrient management options in Inceptisols of semiarid India.

monoculture crop and/or intercrop (Singh et al., 2002). With an area of 8.0 Mha, total production is merely 7.5 million Mg, which is projected to increase to 18.0 million Mg by 2025. Soybean has the potential to bridge the gap between the demand and supply of edible oils and protein. It can also fix N at the gross rate of 125–150 kg N ha^{-1} (Chandel et al., 1989), enhance N stock, and improve soil physical and chemical properties (Saraf and Patil, 1995). Leaf fall during crop development and input through nodulated roots may contribute up to 40 kg N ha^{-1} (Buresh and De Datta, 1991). A positive yield trend over time is observed with better nutrient management (Fig. 5.9A).

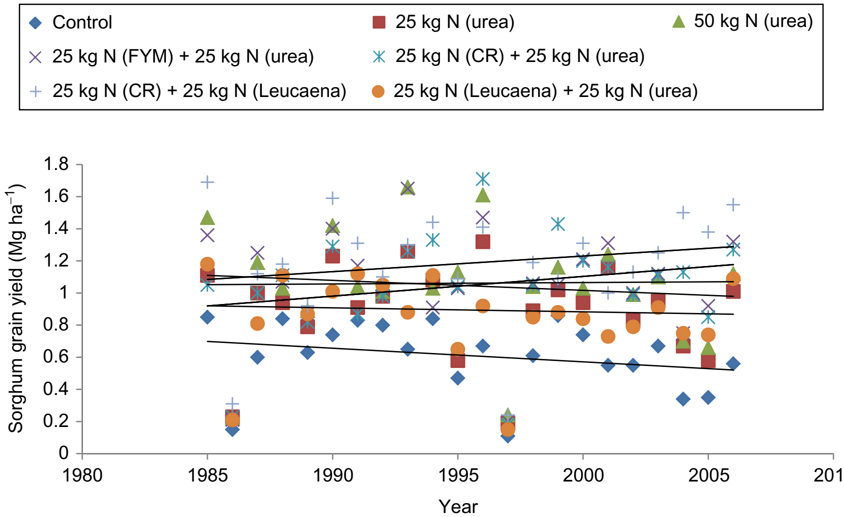

Figure 5.8 Time series yield trends of winter sorghum during 22 years with different nutrient management options in Vertisols of SAT India.

4.1.7 Pearl millet

A rotation based on cereal–legume–nonedible oilseeds is profitable in the extreme semiarid part of Gujarat, India (Vittal et al., 2003). Pearl millet, the fourth most important crop in India, is traditionally a component of the dryland system and is grown in soils of low inherent fertility. The pearl millet-based production system covers 9.8 Mha under tropical conditions of India (FAO, 2008). It can be grown under extremely dry and arid conditions. Low and decreasing yield over time is a concern that is depicted by a negative slope of the trend line (Fig. 5.10A–C).

4.1.8 Other dryland crops

Safflower, another important oilseed crop of India, is cultivated in winter (*Rabi*) season from September/October to February/March. India accounts for 41% (0.3 Mha) of world area under safflower. Because of low yield (630 kg ha^{-1}), safflower production of merely 0.19 million Mg is only 29% of global production followed by that in the United States (17%), Argentina (13%), and Kazakhstan (12%; The Hindu, 2010). It is generally preceded by a short-duration legume such as soybean or mung bean (*Phaseolus mungo*) during the rainy season from June to September. It is grown as a monocrop on residual soil moisture in a 2-year rotation involving chickpea (*Cicer arietinum*) or sorghum. Similarly, other important rainfed crops like cluster bean (*Cyamopsis tetragonoloba*) and castor (*Ricinus communis*)

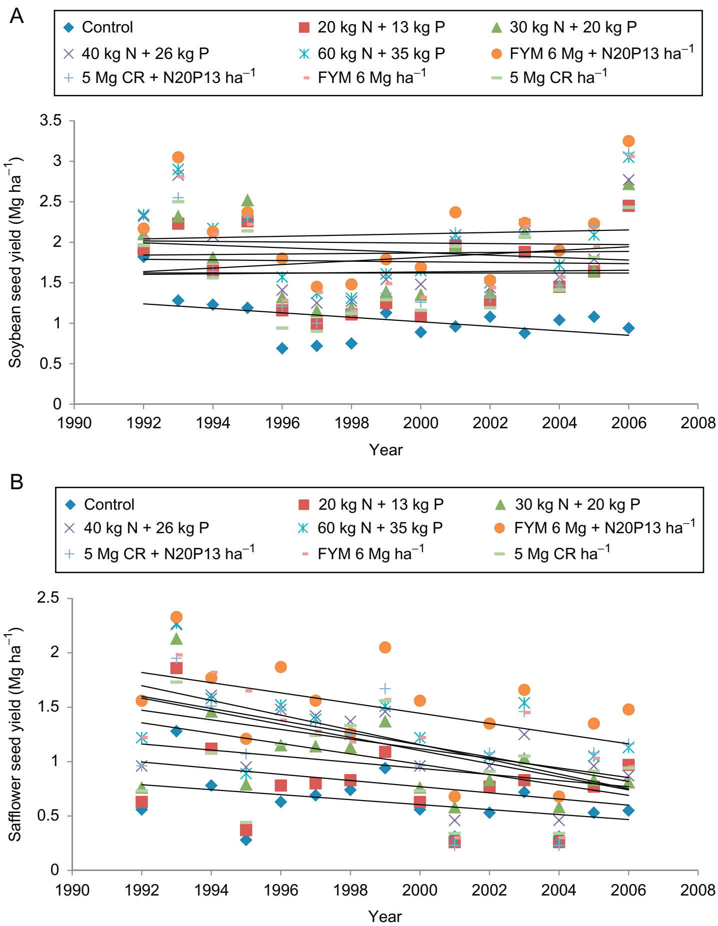

Figure 5.9 Time series yield trends of rainfed (A) soybean and (B) safflower under soybean–safflower sequence during 15 years with different nutrient management options in Vertisols of semiarid India.

in conjunction with INM play a major role in yield sustainability and yield trends (Figs. 5.9A and 5.10A and B).

5. PRODUCTIVITY CONSTRAINTS IN RAINFED ECOSYSTEM

Unlike irrigated agriculture, the productivity of rainfed crops has remained low with some exceptions. Low yields under rainfed conditions

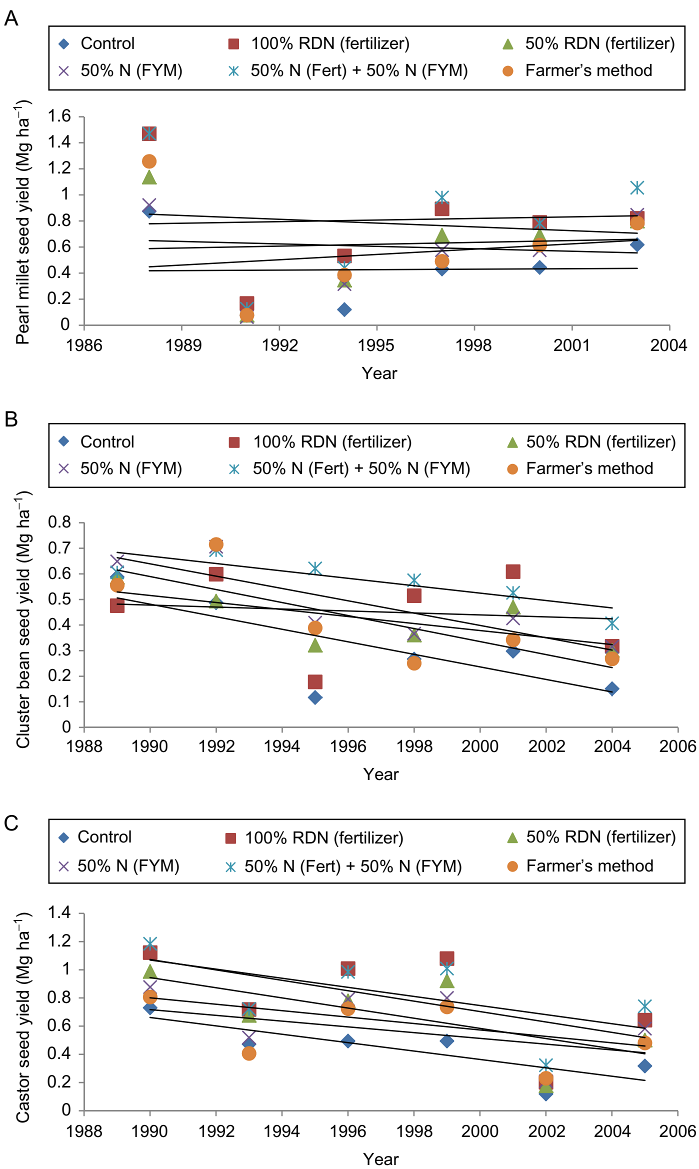

Figure 5.10 Time series yield trends of rainfed (A) pearl millet (B) cluster bean, and (C) castor under pearl millet–cluster bean–castor rotation during 18 years with different nutrient management options in Entisols of semiarid India.

are attributed to several constraints ranging from soil-related to those of marketing. Such constraints are responsible for low biomass production, less root biomass, and low or no residue recycling with the attendant low levels of SOC concentration in soils under rainfed agriculture. Principal constraints to achieving higher productivity of rainfed crops are briefly discussed below.

5.1. Uncertain rainfall

Due to highly variable and uncertain rains (Fig. 5.1), agriculture in rainfed regions depends on the amount and distribution of monsoons. Increased frequency of droughts is a major challenge to rainfed agriculture. Prolonged moisture stress at critical growth stages results in lower productivity.

5.2. Degraded soils

Degraded soils with high risks of accelerated erosion resulting in loss of fertile surface soil and SOC are major constraints. The magnitude of soil loss ranges from 5 to 150 Mg ha^{-1}year^{-1} depending upon soil type, vegetation, and slope gradient. There have been several estimates of area of degraded/waste lands by different organizations. These estimates have been harmonized by adopting spatial data integration with geographical information system for different environment (Maji, 2007). The total degraded area is estimated at 120.72 Mha, of which 104.19 Mha (86.3%) is arable land, and 16.53 Mha (13.7%) is open forest land. Of the total degraded land area, 73.27 Mha (60.7%) is caused by water erosion, 12.40 Mha (10.3%) by wind erosion, 5.44 Mha (4.5%) by salinization, and 5.09 Mha (4.2%) by soil acidification. Some areas are affected by more than one degradation progress (Maji, 2007).

5.3. Low input application

Use of production inputs like fertilizers, supplemental irrigation, good quality seeds, pesticides, and herbicides are lower in rainfed than in irrigated crops. Thus, productivity of rainfed crops has remained low. Although it has been amply demonstrated that soils in rainfed regions are multinutrient deficient, balanced use of these inputs in rainfed crops is rarely achieved. There are wide disparities of inputs between irrigated and rainfed regions due to numerous uncertainties in the crop production.

5.4. Biotic stresses

Yield losses of several rainfed crops, in general, and of pulses, in particular, are high due to severe incidence of diseases and insect pests. In some cases, an entire crop is lost because of severe infestation. Though technological and

management options are well established, they are seldom practiced because of economic and other human dimensions.

5.5. Untapped water-nutrient synergy

Rainfed regions often suffer from water scarcity and are characterized by multinutrient-deficient soils. However, applying plant nutrients in synergy with profile moisture storage is crucial in improving crop productivity and enhancing nutrient and water use efficiencies.

5.6. Poor crop management

Untimely sowing, lack of weeding and supplemental irrigation, and sub-optimum plant population result in poor crop stand. Excessive weed infestation can smother growth of the crops and severely reduce their productivity. Yet, a judicious crop management can substantially enhance productivity, and improve agronomic/economic returns.

5.7. Lack of focused extension program

Improved and short-duration varieties and matching production technologies are available for rainfed cropping. However, the lack of a focused extension program specially aimed at rainfed regions and slow adoption of RMPs are among the major constraints.

5.8. Lack of appropriate policy support

Many coarse grains like finger millet, sorghum, pearl millet, and others do not have a fair price policy. Yet, these crops are highly nutritious and an important component of diet. Farmers are not motivated to apply fertilizers and other inputs because of low monetary returns.

6. STRATEGIES OF SOIL QUALITY MANAGEMENT

Maintaining or enhancing the SOC stock is the most potent weapon in fight against soil degradation and ensuring sustainability of agriculture in dryland area. Consequences of depletion of SOC concentration and stock are poor soil physical quality, loss of favorable biology, and occurrence of multiple nutrient deficiencies. In the rainfed arid, semiarid, and subhumid regions, next to poor rain water management, depletion of nutrients caused by low SOC stock is an important cause of soil degradation. Improving SOC stock is, therefore, crucial in the sustenance of soil quality and enhancing agricultural productivity.

Results of long-term fertilizer experiments, continued for almost 30 years, proved beyond doubt that organic manures are necessary to sustaining the productivity besides improving the SOC stock (Srinivasarao et al., 2009b). However, maintenance of SOC is difficult in drylands as the extent of C loss is rapid due to high temperatures, and the fact that at least four times higher organic matter inputs are required in tropical regions than in temperate environments to maintain the SOC concentration (Srinivasarao, 2011; Srinivasarao et al., 2011a,b,c,d, 2012a,b,c). A number of organic resources are available in India such as farmyard manure (FYM), CRs, livestock dung, and green leaf manures (GLMs). However, under dryland conditions, process of organic matter decomposition is faster, and organic matter disappears rapidly. Therefore, frequent and large quantities of organic manure additions are essential to maintain SOC concentration. To achieve this in different rainfed regions, a range of INM options are being followed based on locally available organic resources. Building up or depletion of SOC stock under these INM practices and understanding its dynamics under various rainfed production systems will lead to sustainable management of SOC and reduce the risks of soil degradation.

SOM is the storehouse of many plant nutrients and it strongly influences the biological activity and productive capacity of soils. Over the years, efforts have been made to improve SOM status in continuously cropped soils by fertilization, manuring, and residue management practices. Experiments conducted on 21 locations across rainfed regions of the country covering eight production systems revealed that most soils are low in SOC concentration (Fig. 5.11), available N, low to high in available P, K, and S. Many soils under farmers' fields are deficient in available Mg, Zn, and B besides NPK which are under continuous cultivation of cotton, groundnut, sunflower, sorghum, maize, pigeon pea, black gram (*Vigna mungo*), green gram (*Vigna radiata*), chickpea, vegetables, fruit crops, etc. Therefore, crop and soil management practices have to be adapted and fine-tuned to ensure long-term crop/cropping systems that add organic matter to the soil. Application of plant nutrients and organic amendments and inclusion/cultivation of legumes favor improvement of soil fertility and sustainability. This is directly related to maintaining the quantity of SOM, which is a critical component of soil productivity. However, resource-poor farmers in dryland regions apply meager quantity of nutrients, and thus crops suffer from multinutrient deficiencies. The best option seems to be integration of farm-generated organic manure with inorganic fertilizers

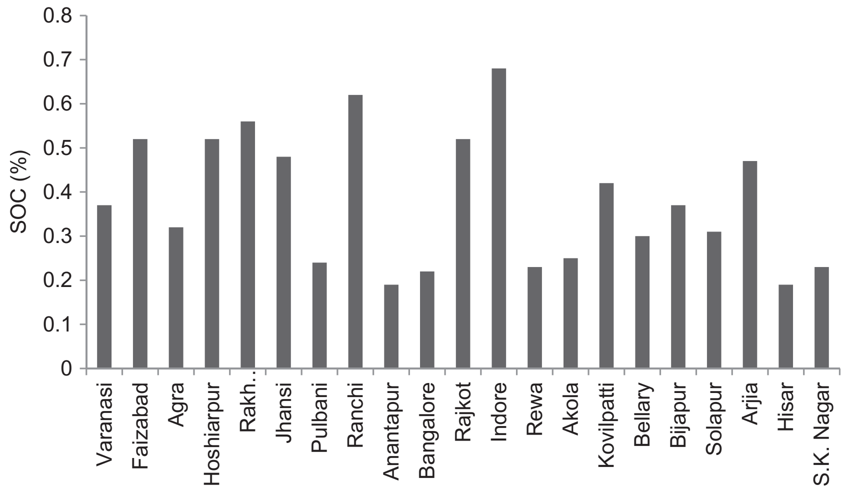

Figure 5.11 Rainfed regions in arid and semiarid tropical India are low in soil organic carbon (Srinivasarao and Vittal, 2007).

in order to enhance SOM and improve productivity and sustainability of dryland agriculture. Crop rotation, residue management, and fertilization can help to maintain the level of SOM. The availability of organic CRs is a major problem in India due to their competing uses but some products such as gliricidia, vermicomposting, tank silt, cover crops, and locally available organic resources like groundnut shells (GNS) as, for example, at Anantapur, are available for soil application as they do not have other major alternate uses. Though chemical fertilization has demonstrable effects on yields, poor farmers in rainfed regions also rely on FYM and other organic manures because of the economic factor. Therefore, using combination of inorganic fertilizers and organic manures (INM) is the best option for long-term sustainability of soil productivity. Besides controlling soil erosion and reducing loss of fertile top soil, increasing SOC concentration and improving soil fertility are possible through adoption of soil and water conservation measures. During the 1960s and 1970s, physical structures like bunding were emphasized, but the focus shifted to field- and community-based *in situ* conservation practices since 1990s. The principal aim of these practices is to reduce or prevent either water or wind erosion, while conserving soil moisture for crop production. Based on past experiences, a range of soil and water conservation measures have been found promising for diverse ecoregions in India (Tables 5.5 and 5.6), and which are effective in reducing losses of soil and SOC stock.

Table 5.5 Recommended soil and water conservation measures for various rainfall zones in India controlling water, soil, carbon, nutrient losses from crop lands

Seasonal rainfall (mm)			
<500	500–700	750–1000	>1000
Contour cultivation with conservation furrows	Contour cultivation with conservation furrows	BBF (Vertisols)	BBF (Vertisols)
Ridging	Ridging	Conservation furrows	Field bunds
Sowing across slopes	Sowing across slopes	Sowing across slopes	Vegetative bunds
Mulching	Scoops	Tillage	Graded bunds
Scoops	Tide ridges	Lock and spill drains	Chos
Tied ridges	Mulching	Small basins	Level terraces
Off-season tillage	Zingg terrace	Field bunds	
Interrow water	Off-season tillage	Vegetative bunds	
Harvesting system	BBF	Graded bunds	
Small basins	Interrow water	Nadi	
Contour bunds	Harvesting system	Zingg terrace	
Field bunds	Small basins		
Khadin	Modified contour bunds		
	Field bunds		
	Khadin		

Source: Vittal et al. (2003)

Table 5.6 Improvements in physical parameters in watershed projects in various agroclimatic conditions ($n = 37$)

Parameter/agro climate	Arid	Semiarid	Humid
Rise in water table (m)	1.05	1.57	1.38
Reduction in runoff (%)	35.0	33.2	30.5
Reduction in soil erosion (%)	15.0	28.8	25.6
Surface water resources developed (%)	9.0	18.0	20.5
Increase in afforestation (%)	10.0	11.3	21.7
Increase in cropping intensity (%)	6.0	16.0	18.3
Increase in employment (%)	12.5	25.0	20.8

Source: Venkateswarlu et al. (2012)

7. NUTRIENT MANAGEMENT

Nutrient management is one of the important aspects of sustainable crop production in dryland farming and of maintaining soil quality. The

strategy of integrated plant nutrient supply (IPNS) adapts plant nutrition to specific farming systems and the desired "yield target" with consideration of improving the resource base, diversifying available plant nutrient sources, and addressing the socioeconomic factors. Further, since plant nutrients are transferred in cyclical processes, IPNS strategy also involves monitoring all pathways of flow of plant nutrients in agricultural production systems to maximize profit, sustain the farming profession, and ensure food production. Thus, IPNS encompasses a holistic approach to nutrient management for crop production, and involves judicious combination of fertilizers, biofertilizers, organic manures (FYM, compost, vermicompost, biogas sludge), green manures, CRs, etc., and of growing legumes in the cropping systems (Prasad, 2008). The IPNS also encompasses balanced fertilization and site-specific nutrient management (SSNM). Yield improvement in some of the important crops like cotton was demonstrated in a farmer's field in India (Fig. 5.12). Considerable research on IPNS has been done in India. Moreover, long-term fertilizer experiments have shown that addition of organic manures in addition to NPK (add-on series) results in high yields over a long period of time as compared to a decline in yield over time when only inorganic

Figure 5.12 Impact SSNM in Bt cotton in Vertisols of Andhra Pradesh, India.

fertilizers are applied (Swarup, 2002). Sarkar and Singh (2002) reported that for soybean–wheat cropping system in the acidic soils of Ranchi (pH < 5.4), soybean yield (averaged over 28 years) was 0.33 Mg ha^{-1} and wheat yield was 0.43 Mg ha^{-1} for plots receiving N alone as compared to 1.59 Mg ha^{-1} for soybean and 2.65 Mg ha^{-1} for wheat when NPK was applied. Application of FYM with NPK increased the soybean yield to 1.86 Mg ha^{-1} and that of wheat to 3.19 Mg ha^{-1}. Further, the effects of NPK + FYM were at par with NPK + lime, implying that in acid soils continuous application of FYM can also partially offset soil acidity.

Data from "replacement series" trials under the Project Directorate of Cropping Systems Research reveal that in most cropping systems (e.g., rice–wheat and rice–rice), application of 50% N through green manure, FYM, or CRs, and 50% through recommended dose of fertilizer (RDF) to summer rice and 100% RDF to winter crop (rice/wheat) gave the same yield as obtained with 100% RDF to both crops. These results show that 25% of NPK fertilizers being used can be saved. However, inferences in such studies are mostly based on agronomic yields, and the results are reported without accounting for NPK added through organic manures and without due consideration of the interaction effects.

Green manure crops have the intrinsic potential to recycle considerable quantities of organic materials and nutrients. It has been observed that green manuring with *Sesbania* adds/recycles large quantities of NPK as compared to other green manures and on equivalent weight basis of FYM. In comparison, addition of wheat straw adds the least amount of NPK. Further, use of *Sesbania* or cowpea (*Vigna unguiculata*) and mung bean residue can produce the same grain yield of rice + wheat without any N application to rice, as obtained with 120 kg N ha^{-1} applied to rice in the control plot (Mandal et al., 2003). Further, productivity of rice–wheat cropping could be raised by 1.2 Mg ha^{-1} with 80 kg N ha^{-1} applied to rice over 120 kg N ha^{-1} applied in control plots (no green manure, residue, or FYM). Use of FYM and *Leucaena* loppings produced lower yields than with application of *Sesbania* or cowpea green manure, or with incorporation of mung bean residue incorporation. Although incorporation of wheat straw is the least effective, it can produce more grain yield than the control (Prasad, 2009).

Legumes are the most important component of IPNS. They may be grown as a green manure, grain crop, or as a dual-purpose crop (grain as well as green manure) within cropping systems. Soil restoring capacity of legumes has been known in India since prehistoric times (Ali et al., 2002) even when their capacity to fix N was not known. Legumes fix 50–500 kg N ha^{-1} depending upon the crop and its growth period (Srinivasarao et al.,

2003) and leave a residual N varying from 30 to −70 kg N ha^{-1} to the succeeding crop (Srinivasarao et al., 2003). Thus, there is a saving of 5.6–39.1 kg N ha^{-1} in wheat following mung bean or black gram. The N saving in wheat decreases as the level of N application increases. It is estimated that in India legumes fix about 2.4 Tg (Tg = teragram = 10^{12} g = 1 million metric ton) of N annually (Singh et al., 2006).

Green manures contribute 60–120 kg N ha^{-1} to the succeeding crop (Srinivasarao et al., 2003). In a study on a sodic soil, green-manured crop supplied with 75 kg N + 30 kg P_2O_5 + 25 kg K_2O ha^{-1} produced same grain yield as the one receiving 180 kg N + 90 kg P_2O_5 + 75 kg K_2O + 5 kg Zn ha^{-1}, showing that benefits of green manuring are not limited to N only (Swarup, 1998). Despite such encouraging results, the area under green manure crops has been declining, mainly because of the nonremunerative nature of these crops. A better alternative is a dual-purpose legume such as cowpea or mung bean. When mung bean is grown as a summer catch crop and its residue is incorporated in the soil after one picking of pods (giving about 0.5 Mg ha^{-1} grain), it contributes N equivalent to 60–90 kg ha^{-1} to the cropping system (Prasad, 2009). Organic manures also supply small amounts of N but when applied regularly over a long time, can overcome the micronutrient deficiencies. Application of organic manures also improves soil physical, chemical, and biological properties.

Biofertilizers (*Rhizobium*, *Azotobacter*, *Azosprillum*, blue-green algae, azolla, phosphate solubilizing organisms, vesicular arbuscular mycorrhiza) can become an important component of IPNS, specially dryland agriculture, where only low levels of fertilizers are applied. Organisms accelerating the decomposition of CRs are also important to enhancing soil fertility (Rao and Patra, 2009).

8. CARBON STOCK OF DRYLAND SOILS AND ITS MANAGEMENT

Organic, inorganic, and total C stocks in soil vary between and within soil types (Fig. 5.13). Vertisols and associated soils contain higher C stocks, followed by Inceptisols < Alfisols < Aridisols. In general, concentration of SOC is more than that of soil inorganic C (SIC) in Alfisols and Aridisols, while SIC is more than SOC in Vertisols and Inceptisols. The SOC stocks (Mg ha^{-1}) range from 26.7 to 59.7 with a mean of 43.7 in Inceptisols, 23.3 to 49.8 with a mean of 30.8 in Alfisols, 28.6 to 95.9 with a mean of 46.4 in Vertisols and 20.1 to 27.4 with a mean of 23.7 Aridisols. The stabilizing effect of clay particles on SOM decreases in the order allophone > amorphous minerals > smectite > illite > kaolinite

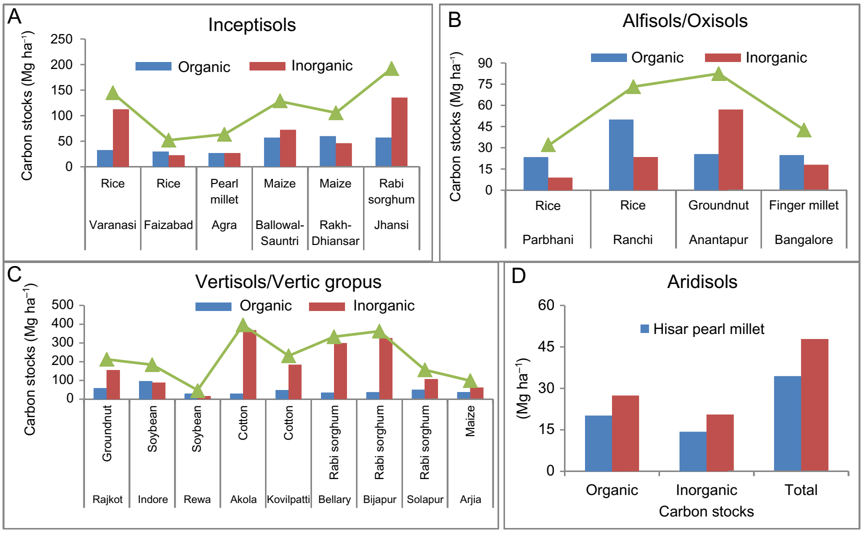

Figure 5.13 (A–D) Organic, inorganic, and total carbon stocks in topical soils of India (Srinivasarao et al., 2009a) (A) Inceptisols, (B) Alfisols/Oxisols, (C) Vertisols/Vertic subgroups, (D) Aridisols.

(Van Breeman and Feijtel, 1990). Vertisols with smectite as dominant mineral contain larger SOC stocks than illitic Inceptisols and kaolinitic Alfisols (Srinivasarao et al., 2009b).

Similarly, SIC concentration and stock vary widely among the soil types. Vertisols contain larger SIC stock followed by Inceptisols, Alfisols, and Aridisols. The SIC stocks (Mg ha^{-1}) range from 22.3 to 135.1(mean 69.1) in Inceptisols, 8.8 to 57.0 (mean 26.8) in Alfisols, 16.0 to 367.6 (mean 178.1) in Vertisols, and 14.3 to 20.5 (mean 17.4) in Aridisols. In most cases, SOC is more in surface than in subsoil layers, while the reverse is the trend with SIC. Total carbon stocks (TCS, Mg ha^{-1}) range from 52.1 to 192.1 (mean 112.8) in Inceptisols, 32.1 to 82.43 (mean 57.6) in Alfisols, 44.7 to 396.2 (mean 224.5) for Vertisols, 34.4 to 47.9 (mean 41.1) in Aridisols. The TCS is also high in Vertisols, followed by Inceptisols, Alfisols, and Aridisols.

The SOC stock mostly depends on climate, soil type, and land use (Dalal and Mayer, 1986). Wani et al. (2003) reported a high rate of C sequestration in Vertisols with pigeon pea-based systems cultivated with improved management options (32 kg C ha^{-1} year^{-1}) as compared to sorghum-based systems with farmer's management. The rate of SOC sequestration measured in

soils of India are lower than those reported from soils of the tropics elsewhere by Dalal and Mayer (1986), Dalal (1989), Murphy et al. (2002), and Young et al. (2005). Low stocks and rate of SOC sequestration in soils of India are attributed to high rates of oxidation of SOM due to high temperature in tropics and frequent cultivation (Dalal and Chan, 2001; Wani et al., 2003). Young et al. (2005) reported that Vertisols with high clay content may contain higher TCS than other soils. Sahrawat (2003) observed that $CaCO_3$ is a common mineral in soils of the dry regions, stretching from subhumid to arid zones, as soils of this region are calcareous in nature. Calcareous soils in India occupy about 230 Mha and constitute 69% of the total geographical area of India (NBSS and LUP, 2008). Further, the SIC stock consists of primary or lithogenic inorganic carbonates and secondary or pedogenic inorganic carbonates. The reaction of atmospheric carbon dioxide (CO_2) with water (H_2O) and calcium (Ca^{2+}) in the upper horizons of the soil, leaching into the subsoil and subsequent reprecipitation, results in formation of secondary carbonates and in the sequestration of atmospheric CO_2 (Lal, 1997). Therefore, subsoil layers contain higher SIC stock than surface soils in most profiles (Sahrawat, 2003).

8.1. Soil carbon stocks in relation to production system

Stocks of SOC, SIC, and TCS differ among production systems and soil types (Fig. 5.13A–D). The SOC stock (Mg ha^{-1}) is generally more in soybean-based production system (62.31) followed by that in maize-based (47.6) and groundnut-based (41.7) systems. Pearl millet and finger millet-based systems contain low SOC stocks. In comparison, soils under cotton-based systems contain more SIC (275.3). Furthermore, soils under postrainy season sorghum production system (243.7) primarily on Vertisols and associated soils also contain high levels of SIC. In comparison, soils under rice-based systems contain the least SIC stock (18.2). The highest TCS are observed in soils under cotton-based production system, followed by those in summer sorghum-based and the least in pearl millet-based systems. However, % contribution of SOC to TSC is higher under rice-based system, while the highest contribution to TCS is in cotton-based system. On a regional scale, above- and below-ground biomass production is probably the major determinant of the depth distribution of SOC (Jobbagy and Jackson, 2000). The above-ground biomass has probably only limited effects on SOM levels compared to the below-ground biomass as has been demonstrated by long-term residue management studies (Clapp et al., 2000; Reicosky et al., 2002). The dominant role of root C in soil is also indicated

by greater relative contribution of root versus shoot tissue to the SOC stock (Rasse et al., 2004). Root to shoot ratio of maize ranges from 0.21 to 0.25 in soybean and 0.5 in barley (*Hordeum vulgare*; Allmaroas et al., 2004; Bolinder et al., 1997). Besides root biomass, its composition also impacts the SOC stock. In general, leafy plants decompose faster than the woody plants, and leaves decompose faster than roots (Wang et al., 2004). The second most abundant compounds after proteins are lignins, which largely contribute to terrestrial biomass residues. These compounds exhibit a higher resistance to microbial degradation as compared to celluloses (Martin and Haider, 1986). Suberin is mostly found in root tissues and is a major contributor to SOM (Nierop et al., 2003). Among dryland crops, the lignin concentration is 4% in sorghum plant litter, 8% in soybean, 10% in maize roots, 9–13% in millets,11–13% in rice, and 6–16% in legumes such as alfalfa (*Medicago sativa*; Bilbro et al., 1991; Clement et al., 1998; Devevre and Horwath, 2000; Fernandez et al., 2003; Scheffer, 2002). Corn roots also contain a wide range of fatty acids beside carbohydrates, lignin, lipids, and alkyl aromatics (Gregorich et al., 1996).

Within a soil type, the soil C stock also depends on the production system. In Vertisols and associated series, soils under cotton and sorghum systems contain large SIC stocks, while those under soybean and groundnut systems contain higher SOC stock. Soils under legume-based systems on Vertisols contain higher SOC stocks than those under cereal-based systems in the tropics (Wani et al., 1995, 2003). In Inceptisols, maize-based systems contain large SIC and SOC stocks. In Alfisols, rice-based system (at Ranchi and Phulbani sites) contains relatively higher SOC stock while groundnut-based (Anantapur site) system contains large SIC stock. This trend may be due to larger carbonate deposits in the deeper layers of the profile, frequent addition of gypsum to groundnut, and differences in rainfall, parent base material, and other management practices adapted at these locations. In Aridisols, pearl millet-based systems at S.K. Nagar site contain higher TCS than those at Hisar (Fig. 5.13D).

8.2. Carbon stocks in relation to rainfall

In general, SOC stocks increase with increase in the mean annual rainfall (Fig. 5.14A and B; $r=0.59$, $p<0.05$). In contrast, however, the SIC stocks decrease with the increase in mean annual rainfall, from 156.4 Mg ha^{-1} for rainfall of <550 mm to 26.0 Mg ha^{-1} for >1100 mm. The SIC stocks generally exceed those of SOC, and the TCS decreases with increase in mean

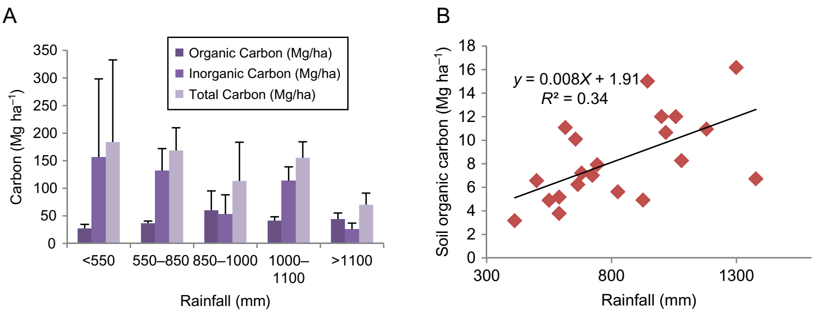

Figure 5.14 (A) Soil carbon stocks in rainfed production systems in relation to rainfall and (B) relationship between mean annual rainfall (mm) and soil organic carbon in surface layer (0–15 cm) under rainfed conditions (SOC stock = 1.91 + 0.008X; R^2 = 0.34*; Srinivasarao et al., 2009a).

annual rainfall from 183.8 Mg ha^{-1} in the arid environment (<550 mm) to 70.2 Mg ha^{-1} in subhumid regions (>1100 mm).

8.3. Carbon enhancing management options

While being the storehouse of many plant nutrients, the SOM also strongly influences the biological activity and productive capacity of soils. Over the years, efforts have been made to improve the SOM status in continuously cropped soils by fertilization, manuring, and residue management practices. However, maintaining and increasing SOM is a major challenge in dryland soils due to high temperature and frequent drought stress. Therefore, crop and soil management practices have to be adapted to ensure long-term crop/cropping systems. Application of plant nutrients (Paustian et al., 1997) and organic amendments and inclusion/cultivation of legumes enhance soil fertility and sustainability. This improvement is directly related to maintaining the quantity of SOM, which is a critical component of soil productivity. However, resource-poor farmers in dryland regions apply meager quantity of nutrients and thus crops suffer from multinutrient deficiencies (Srinivasarao et al., 2003). The best option is integration of farm-generated organic manure with inorganic fertilizers to increase SOM, improve productivity, and enhance sustainability of dryland agriculture. Crop rotation, residue management, and fertilization can maintain the desired level of SOM (Campbell et al., 1992). Ali et al. (2002) reported that by improving physical, chemical, and biological properties of soils, food legume

cultivation could reverse the declining trend in productivity of cereal–cereal systems. The availability of CRs is a major constraint in India due to their competing uses, but in some crops, by-products such as GNS are available for soil application. Though chemical fertilization has a large effect on yields, poor farmers in rainfed regions mostly rely on FYM and other organic amendments because of high cost of chemical fertilizers. Thus, nutrient management and residue incorporation also have a large impact on SOC sequestration.

8.3.1 Agricultural practices

Changes in agricultural management can potentially increase the accumulation rate of SOC sequestration. West and Post (2002) indicated that, on average a change from conventional tillage (CT) to no-till (NT) can sequester $57 \pm 14\ \mathrm{g\ C\ m^{-2}\ year^{-1}}$, excluding wheat-fallow systems. Enhancing rotation complexity can sequester an average $20 \pm 12\ \mathrm{g\ C\ m^{-2}\ year^{-1}}$, excluding a change from continuous corn to corn–soybean. The SOC sequestration rates, with change from CT to NT, can be expected to peak in 5–10 years with SOC reaching a new equilibrium in 15–20 years. Changes in agricultural practices for the purpose of increasing SOC must increase organic matter inputs to the soil, decrease decomposition of SOM and oxidation of SOC, or a combination thereof (Follett, 2001; Paustian et al., 2000).

A range of management options are being promoted by CRIDA in farmer's participatory action mode for diverse soils in rainfed districts of Andhra Pradesh. CR recycling, FYM, biofertilizers, inclusion of legumes in the cropping sequence or as intercrops, green manure crops, GLM, tank silt addition, vermicomposting along with chemical fertilizers are some of the important options to improve soil quality and crop productivity (Srinivasarao, 2011; Srinivasarao et al., 2011a,b,c). Impact of tank silt application in degraded Alfisols of Andhra Pradesh, India indicates strong response of maize and castor yields besides improving soil physical, chemical, and biological properties (Fig. 5.15). Among them, GLM with *Gliricidia* is a promising and climate-friendly technology. *Gliricidia*, commonly known as *Kakawate*, is also used as an insecticide, repellant, and rodenticide and also survives in dry, acidic soils or even on degraded soils under rainfed conditions. Green leaf manuring is an important practice for increasing SOC stock. Degraded soils of the tropics lack sufficient amount of N. Growing *Gliricidia* plants on farm bunds serves dual purpose of producing GLM rich in N and also protects soil against erosion (Srinivasarao

Figure 5.15 Application of tank silt in the field (A), performance of maize without (left) and with (right) tank silt application in low fertile red soils of Rangareddy district (B), (C) castor performance with (right) and without (left) application of tank silt in Mahbubnagar.

et al., 2011b). Farm bunds can be used for growing N fixing shrubs and trees to generate nutrient-rich loppings. For example, growing *Gliricidia* at a close sparing of 75 cm on farm bunds could provide 28–30 kg N ha^{-1} $year^{-1}$ in addition to a valuable organic matter (Wani et al., 2009). Use of INM can improve soil quality for enhancing water use efficiency and increasing farm income. Farmers should, therefore, be

encouraged to grow *Gliricidia* on farm bunds and field borders for use in crop production, which is a sustainable means of maintaining soil fertility along with inorganic sources of nutrients.

8.3.2 Improvement of crop yield through **Gliricidia** *green leaf manuring*

Enhancement of soil productivity and increase in crop yields are obtained with the addition of *Gliricidia* leaf manuring in several rainfed crops. Impact of mulch-cum-manuring with *Gliricidia* can increase castor yield by 300% in comparison with control and 150% in comparison with FYM and use of chemical fertilizer (Srinivasarao et al., 2011b). Application of *Gliricidia* leaf manuring has increased yields of different rainfed crops in many regions such as that of finger millet in red (Alfisols) soils of Karnataka, groundnut in red soils of Andhra Pradesh, pearl millet in light textured soils of Gujarat, and sorghum in medium to deep black (Vertisols) soils of Maharashtra (AICRPDA Annual Report, 2010). At Bhubaneswar, in acid red and lateritic (Ultisols) soils, grain yield of maize improved from 1.7 to 2.1 Mg ha^{-1} by *Gliricidia*-GLM equivalent to 20 kg N ha^{-1} (AICRPDA Annual Report, 2007). In long-term manurial experiment on Alfisols of CRIDA farm near Hyderabad, sorghum and green gram yields were significantly higher with the addition of 1–2 Mg of *Gliricidia* along with 10–20 kg N ha^{-1} (Sharma et al., 2004). Sharma and colleagues reported that two INM treatments, 2 Mg of *Gliricidia* loppings + 20 kg N and 4 Mg compost + 20 kg N can increase the sorghum grain yield by 84.6% and 77.7% over control, respectively. However, the highest SOC concentration (0.74%) was observed in 100% organic treatment (4 Mg compost + 2 Mg *Gliricidia* loppings). Some of these options of managing nutrients by using farm-based organics can also form a potential component of organic farming. For example, Sharma et al. (2002) reported that the conjunctive use of urea and organics such as loppings of *Leucaena* and *Gliricidia* (1:1 ratio on N equivalent) can increase sorghum grain yield to about 1.7 Mg ha^{-1}, and provide about 50% N requirement of sorghum through farm-based organic sources. This strategy can be used to supplement fertilizer N by 50% by using green loppings of *Gliricidia* and *Leucaena* for growing organic produce. Further, SOC concentration is also improved by application of CRs such as sorghum stover and *Gliricidia* at 2 Mg ha^{-1} under minimum and CT in sorghum–castor rotation in rainfed Alfisols. Sharma and colleagues also reported that increase in N levels from 0 to 90 kg ha^{-1} also increased SOC concentration over a period of 8 years.

8.4. Experiences from long-term experiments

Seven ongoing long-term experiments involving permanent manurial and INM experiments conducted under the auspices of the All India Coordinated Research Project on Dryland Agriculture (AICRPDA) are sited in six ecoregions in semiarid climates at Anantapur (Andhra Pradesh), Bangalore (Karnataka), Solapur (Maharashtra), Indore (Madhya Pradesh), Sardar Krushinagar (Gujarat), and Varanasi (Uttar Pradesh). Details of the soil type, cropping systems, and ecoregional characteristics are outlined in Table 5.7. Common treatments across seven experiments are control (no fertilizer or organics), 100% RDFs, 50% RDF + 50% organics, and 100% organics (Srinivasarao et al., 2011d; Srinivasarao et al., 2012a,b,c,d,e,f). All treatments at each site have been laid out in triplicate according to a randomized block design. The results of these experiments are briefly presented below.

8.4.1 Crop yield improvement through better nutrient management practices

Soil fertility management treatments produced significantly higher mean yield compared with that of the control (Table 5.8). Higher yields were obtained with the use of organic manure in combination with chemical fertilizers. For example, higher mean pod yield of groundnut (Mg ha^{-1}) was obtained in 50% RDF + FYM 4 Mg ha^{-1} (1.03) followed by 50% RDF + 4 Mg ha^{-1} GNS (1.02), 100% RDF (0.98), and the least in the control (0.78). In case of groundnut–finger millet rotation, higher mean pod yield (1.34 Mg ha^{-1}) of groundnut was obtained with the application of FYM followed by FYM + 50% NPK (1.22 Mg ha^{-1}), FYM + 100% NPK (1.10 Mg ha^{-1}), recommended NPK (0.72 Mg ha^{-1}), and the least in control (0.40 Mg ha^{-1}). In contrast, higher grain yield (Mg ha^{-1}) of finger millet was obtained through the application of FYM + 100% NPK (3.96) followed by FYM + 50% NPK (3.77), FYM (3.25), recommended NPK (2.58), and the least in the control (0.82). In finger millet monocropping, higher mean grain yields (Mg ha^{-1}) over 27 cropping seasons of 3.28 were obtained through integrated use of RDF along with FYM 10 Mg ha^{-1} followed by 2.92 with FYM 10 Mg ha^{-1} + 50% NPK. Even with the application of FYM 10 Mg alone, sustained and significantly higher grain yield was obtained compared with that from the sole application of chemical fertilizer or unfertilized control. In case of sorghum, for the entire 22-year period, higher grain yield (1.2 Mg ha^{-1}) was obtained through the application of 25 kg N (CR) + 25 kg N (*Leucaena*), and it was on par with 25 kg N

Table 5.7 Details of location, soil type, production system, and selected carbon management option included in the present study (Srinivasarao et al., 2009a)

Location/ state/soil type	Crop/cropping system	Latitude, longitude, and altitude	Climate/ annual rainfall (mm)	Treatment details
Anantapur Andhra Pradesh Alfisols	Monocropping of groundnut 1985–2004 (20 years)	14°42′ N, 77°40′ E, 350 m	Semiarid (566)	T_1 = control (no fertilizer), T_2 = 100% recommended dose of fertilizer (RDF) (20:40:40 N, P_2O_5, K_2O), T_3 = 50% RDF + 4 Mg groundnut shells (GNS) ha^{-1}, T_4 = 50% RDF + FYM 4 Mg ha^{-1}, T_5 = 100% organic (FYM 5 Mg ha^{-1})
Bangalore Karnataka Alfisols	Finger millet–finger millet	12°46′ N, 77°11′ E, 810 m	Semiarid (768)	T_1 = control, T_2 = FYM 10 Mg ha^{-1}, T_3 = FYM 10 Mg ha^{-1} + 50% NPK, T_4 = FYM 10 Mg ha^{-1} + 100% NPK, T_5 = recommended NPK (50:50:25 kg NPK ha^{-1}–finger millet)
Bangalore Karnataka Alfisols	Groundnut–finger millet rotation	12°46′ N, 77°11′ E, 810 m	Semiarid (768)	T_1 = control, T_2 = FYM 10 Mg ha^{-1}, T_3 = FYM 10 Mg ha^{-1} + 50% NPK, T_4 = FYM 10 Mg ha^{-1} + 100% NPK, T_5 = recommended NPK (25:50:25 kg NPK ha^{-1}–groundnut, 50: 50:25 kg NPK ha^{-1} –finger millet)
Solapur Maharashtra Vertisols	Winter sorghum	17°51′N, 75°32′E, 480 m	Semiarid (723)	T_1 = control, T_2 = 25 kg N ha^{-1} (urea), T_3 = 50 kg Nha^{-1} (urea), T_4 = 25 kg N ha^{-1} through sorghum residue (CR), T_5 = 25 kg N ha^{-1} through FYM, T_6 = 25 kg N ha^{-1} (CR) + 25 kg N ha^{-1} (urea), T_7 = 25 kg N ha^{-1} (FYM) + 25 kg N ha^{-1} (urea), T_8 = 25 kg N ha^{-1} (CR) +

				25 kg N ha^{-1}(*Leucaena* clippings), $T_9 = 25$ kg N ha^{-1} (*Leucaena*), $T_{10} = 25$ kg N ha^{-1} (*Leucaena*) + 25 kg N ha^{-1} (urea)
S.K. Nagar Gujarat Entisols	Pearl millet–cluster bean–castor rotation (once in 3 years)	24°30′N, 72°13′E, 152.5 m	Semiarid (550)	$T_1 =$ control, $T_2 = 100\%$ recommended dose of N through mineral fertilizer (RDNF), $T_3 = 50\%$ RDNF, $T_4 = 50\%$ recommended N (FYM), $T_5 = 50\%$ recommended N (fertilizer) + 50% recommended N (FYM), $T_6 =$ farmers method (5 Mg of FYM ha^{-1} once in 3 years)
Indore Madhya Pradesh Vertisols	Soybean–safflower sequence	22°51′N, 75°51′E, 530 m	Semiarid (900)	$T_1 =$ control, $T_2 = 20$ kg N + 13 kg P, $T_3 = 30$ kg N + 20 kg, $T_4 = 40$ kg N + 26 kg, $T_5 = 60$ kg N + 35 kg P, $T_6 =$ FYM 6 Mg $ha^{-1} + N_{20}P_{13}$, $T_7 = 5$ Mg soybean residue $ha^{-1} + N_{20}P_{13}$, $T_8 =$ FYM 6 Mg ha^{-1}, $T_9 = 5$ Mg soybean residues ha^{-1}
Varanasi Uttar Pradesh Inceptisols	Upland rice–lentil sequence	25°11′N, 82°51′E, 480 m	Subhumid (1080)	$T_1 =$ control, $T_2 = 100\%$ RDF (inorganic), $T_3 = 50\%$ RDF (inorganic), $T_4 = 100\%$ organic (FYM), $T_5 = 50\%$ organic (FYM), $T_6 = 50\%$ RDF + 50% (foliar), $T_7 = 50\%$ organic (FYM) + 50%RDF, $T_8 =$ farmers practice

Table 5.8 Mean crop yield, percentage improvement over control plots, and sustainable yield index (SYI) of different crops in seven long-term experiments under rainfed production systems (Srinivasarao et al., 2011d, 2012a,b,c,d,e,f)

Location/production system	Treatment				
Anantapur (groundnut)	**Control**	**100% RDF**	**50% RDF +4 Mg ha^{-1} GNS**	**50% RDF + FYM 4 Mg ha^{-1}**	**100% organic (FYM 5 Mg ha^{-1})**
Mean yield*	0.78^{D}	0.98^{B} (25.6)**	1.02^{A} (30.8)	1.03^{A} (32.1)	0.92^{C} (17.9)
SYI	0.25^{D}	0.32^{C} (28.0)	0.48^{A} (92.0)	0.46^{A} (84.0)	0.38^{B} (52.0)
Bangalore (groundnut–finger millet)	**Control**	**FYM at 10 Mg ha^{-1}**	**FYM at 10 Mg ha^{-1} + 50% NPK**	**FYM at 10 Mg ha^{-1} + 100% NPK**	**Rec. NPK**
Mean yield					
Groundnut	0.40^{E}	1.10^{C} (175.0)	1.22^{B} (205.0)	1.34^{A} (235.0)	0.72^{D} (80.0)
Finger millet	0.82^{E}	3.25^{C} (296.3)	3.77^{B} (359.8)	3.96^{A} (382.9)	2.58^{D} (214.6)
SYI					
Groundnut	0.09^{D}	0.23^{A} (155.6)	0.24^{A} (166.7)	0.21^{B} (133.3)	0.16^{C} (77.8)
Finger millet	0.24^{E}	0.71^{C} (195.8)	0.80^{A} (233.3)	0.76^{B} (216.7)	0.62^{D} (158.3)
Bangalore (finger millet)	**Control**	**FYM at 10 Mg ha^{-1}**	**FYM at 10 Mg ha^{-1} + 50% NPK**	**FYM at 10 Mg ha^{-1} + 100% NPK**	**Rec. NPK**
Mean yield	0.84^{E}	2.48^{C} (195)	2.92^{B} (248)	3.28^{A} (290)	2.16^{D} (157)
SYI	0.04^{D}	0.58^{B} (1350)	0.62^{A} (1450)	0.59^{B} (1375)	0.36^{C} (800)

Solapur (winter sorghum)	**Control**	**50 kg N ha^{-1} urea**	**25 kg N ha^{-1} CR + 25 kg N ha^{-1} urea**	**25 kg N ha^{-1} FYM + 25 kg N ha^{-1}urea**	**25 kg N ha^{-1} CR + 25 kg N ha^{-1} *Leucaena***	**25 kg N ha^{-1} *Leucaena* + 25 kg N ha^{-1} urea**
Mean yield	0.61^{D}	1.04^{B} (70.5)	1.06^{B} (73.8)	1.05^{B} (72.1)	0.85^{C} (39.3)	1.19^{A} (95.1)
SYI	0.38^{D}	0.41^{C} (7.9)	0.45^{B} (18.4)	0.44^{B} (15.8)	0.48^{A} (26.3)	0.44^{B} (15.8)

S.K. Nagar (pearl millet)	**Control**	**100% recommended dose of N through mineral fertilizer (RDNF)**	**50% RDNF**	**50% recommended N (FYM)**	**50% RDN (F) + 50% RDN (FYM)**	**Farmers method (5 Mg of FYM ha^{-1} once in 3 years)**
Mean yield						
Pearl millet	0.43^{E}	0.78^{B} (81.4)	0.62^{C} (44.2)	0.55^{D} (27.9)	0.81^{A} (88.4)	0.60^{C} (39.5)
Cluster bean	0.32^{E}	0.45^{C} (40.6)	0.43^{D} (34.4)	0.48^{B} (50.0)	0.58^{A} (81.3)	0.42^{D} (31.3)
Castor	0.44^{F}	0.80^{B} (81.8)	0.67^{C} (52.3)	0.63^{D} (43.2)	0.83^{A} (88.6)	0.57^{E} (29.5)
SYI						
Pearl millet	0.14^{E}	0.24^{B} (71.4)	0.22^{C} (57.1)	0.25^{B} (78.6)	0.30^{A} (114.3)	0.16^{D} (14.3)
Cluster bean	0.23^{D}	0.46^{B} (100)	0.36^{C} (56.5)	0.46^{B} (100)	0.69^{A} (200)	0.34^{C} (47.8)
Castor	0.32^{D}	0.40^{B} (25.0)	0.38^{C} (18.8)	0.39^{C} (21.9)	0.46^{A} (43.8)	0.42^{B} (31.3)

Indore (soybean)	**Control**	**20 kg N + 13 kg P**	**30 kg N + 20 kg P**	**40 kg N + 26 kg P**	**60 kg N + 35 kg P**	**FYM 6 Mg ha^{-1} + $N_{20}P_{13}$**	**Soybean residue 5 Mg ha^{-1} + $N_{20}P_{13}$**	**FYM at 6 Mg ha^{-1}**	**Soybean residues at 5 Mg ha^{-1}**
Mean yield									
Soybean	1.04^{E}	1.62^{D} (55.8)	1.76^{C} (69.2)	1.89^{B} (81.7)	1.99^{A} (91.3)	2.10^{A} (101.9)	1.79^{C} (72.1)	1.86^{B} (78.8)	1.63^{D} (56.7)
Safflower	0.63^{G}	0.80^{F} (27.0)	1.02^{D} (61.9)	1.16^{C} (84.1)	1.21^{B} (92.1)	1.49^{A} (136.5)	1.16^{C} (84.1)	1.22^{B} (93.7)	0.97^{E} (54.0)

Continued

Table 5.8 Mean crop yield, percentage improvement over control plots, and sustainable yield index (SYI) of different crops in seven long-term experiments under rainfed production systems (Srinivasarao et al., 2011d, 2012a,b,c,d,e,f)—cont'd

Location/ production system	Treatment								
Indore (soybean)	**Control**	**20 kg N + 13 kg P**	**30 kg N + 20 kg P**	**40 kg N + 26 kg P**	**60 kg N + 35 kg P**	**FYM 6 Mg ha^{-1} + $N_{20}P_{13}$**	**Soybean residue 5 Mg ha^{-1} + $N_{20}P_{13}$**	**FYM at 6 Mg ha^{-1}**	**Soybean residues at 5 Mg ha^{-1}**
SYI									
Soybean	0.41^{C}	0.47^{A} (14.6)	0.46^{A} (12.2)	0.48^{A} (17.1)	0.48^{A} (17.1)	0.48^{A} (17.1)	0.38^{D} (−7.3)	0.42^{B} (2.4)	0.44^{B} (7.3)
Safflower	0.22^{E}	0.29^{D} (31.8)	0.29^{D} (31.8)	0.31^{C} (40.9)	0.31^{C} (40.9)	0.45^{A} (104.5)	0.36^{B} (63.6)	0.38^{B} (72.7)	0.32^{C} (45.5)

Varanasi (upland rice)	**Control**	**100% RDF (inorganic)**	**50% RDF (inorganic)**	**100% organic (FYM)**	**50% RDF + 50% (foliar)**	**50% organic (FYM) + 50% RDF**	**Farmers practice**
Mean yield							
Rice	1.08^{F}	1.85^{B} (71.3)	1.51^{D} (39.8)	1.75^{C} (62.0)	1.57^{D} (45.4)	1.95^{A} (80.6)	1.37^{E} (26.9)
Lentil	0.48^{D}	0.77^{B} (60.4)	0.54^{D} (12.5)	0.82^{B} (70.8)	0.66^{C} (37.5)	1.04^{A} (116.7)	0.51^{D} (6.3)
SYI							
Rice	0.17^{D}	0.25^{B} (47.1)	0.21^{C} (23.5)	0.26^{B} (52.9)	0.22^{C} (29.4)	0.29^{A} (70.6)	0.20^{C} (17.6)
Lentil	0.14^{F}	0.24^{C} (71.4)	0.16^{E} (14.3)	0.26^{B} (85.7)	0.19^{D} (35.7)	0.30^{A} (114.3)	0.15^{F} (7.1)

Different capital letters within rows are significantly different at $P=0.05$.
*Mean yields.
**Percent increase in productivity over control plots.

(FYM) + 25 kg N (urea) (1.06), 25 kg N (CR) + 25 kg N (urea) (1.05), and 50 kg N (urea) (1.04) and was the least in control (0.61). The higher average seed yields (Mg ha^{-1}) of pearl millet (0.81), cluster bean (0.58), castor (0.83) over six cropping seasons were obtained through INM followed by those of 0.78, 0.45, and 0.80 Mg ha^{-1}, respectively, with 100% RDN (fertilizer). For the entire 15-year period, higher grain yield was obtained through the application of FYM 6 Mg + $N_{20}P_{13}$ ha^{-1} (2.10 and 1.49 Mg ha^{-1} for soybean and safflower, respectively) and was the least in the control (1.04 and 0.63 Mg ha^{-1} for soybean and safflower, respectively). Both crops responded well to a higher dose of fertilizer application and also to the integrated use of organics and chemical fertilizers. Significantly, higher yields were obtained through the application of 60 kg N + 35 kg P (as P_2O_5) ha^{-1} (1.99, 1.21 Mg ha^{-1}) compared to that with application of 5 Mg CR + $N_{20}P_{13}$ ha^{-1} (1.79, 1.16 Mg ha^{-1}), FYM 6 Mg ha^{-1}(1.86, 1.22 Mg ha^{-1}), and 5 Mg CR ha^{-1}(1.63, 0.97 Mg ha^{-1}). Pooled data of 21 years suggest a higher grain yield (Mg ha^{-1} of rice and lentil, respectively) through the application of 50% organic (FYM) + 50% RDF (1.95, 1.04) followed by 100% RDF (mineral) (1.85, 0.77) and was on par with 100% organic (FYM) (1.75, 0.82), and the least yield was measured in the control (1.08, 0.48).

The magnitude of increase in yield (Mg ha^{-1}) in comparison with the control was: (1) from 0.78 to 1.03 in groundnut with 50% RDF + FYM 4 Mg ha^{-1}, (2) 0.40 to 1.34 and 0.82 to 3.96 in groundnut and finger millet, respectively, through 10 Mg ha^{-1}FYM + 100% NPK in groundnut–finger millet rotation, (3) 0.84 to 3.28 in finger millet through 10 Mg ha^{-1}FYM + 100% NPK, (4) 0.61 to 1.19 in sorghum through 25 kg N ha^{-1} (*Leucaena* clippings) + 25 kg N ha^{-1} (urea), (5) 0.43 to 0.81, 0.32 to 0.58, and 0.44 to 0.83 in pear millet, cluster bean, and castor, respectively through 50% RDN (fertilizer) + 50% RDN (FYM), (6) 1.04 to 2.10 and 0.63 to 1.49 in soybean and safflower, respectively, through 6 Mg ha^{-1} FYM + 20 kg N + 13 kg P ha^{-1}, and (7) 1.08 to 1.95 and 0.48 to 1.04 in rice and lentil, respectively, through 50% N (FYM) + 50% RDN treatment.

Significantly higher SYI ((SYI = $Y - \sigma)/Y_{\mathrm{m}}$, where Y is the estimated average yield of a practice across the years. σ is its estimated standard deviation, and Y_{m} is the observed maximum yield in the experiment during the years of cultivation) was observed with the application of organic amendments either alone or in combination with chemical fertilizers compared to control or sole application of chemical fertilizer. The SYI of groundnut

was also higher in 50% RDF + 4 Mg ha^{-1} GNS (0.48) followed by 50% RDF + FYM 4 Mg ha^{-1} (0.46), FYM 5 Mg ha^{-1} (0.38), 100% RDF (0.32) and the lowest in control (0.25). The highest SYI was obtained with the application of FYM + 50% NPK (0.24 for groundnut, 0.80 for finger millet) followed by FYM + 100% NPK (0.21 for groundnut, 0.76 for finger millet) in groundnut–finger millet rotation. In case of finger millet monocropping, the highest SYI was observed in FYM 10 Mg ha^{-1} + 50% NPK followed by FYM 10 Mg ha^{-1} + 100% NPK, FYM 10 Mg ha^{-1} and recommended NPK. The highest SYI was obtained with 25 kg N (CR) + 25 kg N (*Leucaena*; 0.48) followed by 25 kg N (CR) + 25 kg N (urea; 0.45) and the lowest in control (0.38). A higher SYI was also obtained with use of FYM or *Leucaena* clippings along with urea which was at par with 25 kg N (CR) + 25 kg N (urea) treatment. The SYI of all three crops was higher in 50% RDN (fertilizer) + 50% RDN (FYM; 0.30 for pearl millet, 0.69 for cluster bean, and 0.46 for castor) followed by 100% RDN (fertilizer) (0.24, 0.46, 0.40), 50% RDN (FYM) (0.25, 0.46, 0.39), 50% RDN (fertilizer) (0.22, 0.36, 0.38), farmer's practice (0.16, 0.34, 0.42), and the lowest in control (0.14, 0.23, 0.32), respectively. Similarly, significantly higher SYI was obtained with the application of organics either alone or in combination with chemical fertilizers compared with either the control or with the sole application of chemical fertilizers at a lower dose in case of safflower. Significantly higher residual effect was observed in FYM compared to that with the use of residues of soybean and safflower. The highest SYI was measured with FYM 6 Mg + $N_{20}P_{13}$ ha^{-1} (0.48 and 0.45 for soybean and safflower, respectively), and the lowest in the control (0.41 and 0.22). The highest SYI (% for rice and lentil, respectively) was observed in 50% organics (FYM) + 50% RDF (29.1, 30.1) followed by 100% organic (FYM) (26.3, 26.1), and the lowest was in control (17.1, 14.1).

8.5. Soil carbon stocks and agronomic productivity

Crop yield sustainability under rainfed conditions depends on improvement in soil quality through increase in SOC stock. The relationships between SYI and SOC concentration and inputs of biomass C indicate that maintenance of SOC concentration through regular organic or mineral inputs determines the sustainability of rainfed production systems. The improvement in SOC stock is also related to an enhanced water-holding capacity (WHC) of the soil profile (Du et al., 2009), which alleviates intermittent droughts, a major constraint in dryland agriculture.

8.5.1 Relationships of SYI to total cumulative C input

A highly significant positive correlation is observed between SYI and total C inputs in groundnut monocropping ($R^2=0.95$, $P<0.001$), finger millet ($R^2=0.87$, $P<0.01$), and sorghum ($R^2=0.76$, $P<0.01$), whereas these relationships are relatively weak in crops like cluster bean, safflower, rice, and lentil. Application of chemical fertilizers alone may not sustain agronomic productivity on a long-term basis. Significantly higher SYI is obtained with the application of organics either alone or in combination with chemical fertilizers compared to control or sole application of chemical fertilizers. Further, application of FYM/CR/GLM significantly improves SYI of both crops compared to use of recommended rate of NPK, probably due to a high WHC in treatments receiving organic amendments. Thus, increase in soil moisture storage by application of FYM is important to obtaining high yields under rainfed conditions. Ghosh et al. (2006) reported that total system productivity was 130% higher in a groundnut-based (rainy season groundnut followed by other post rainy season crops viz., groundnut, chickpea, wheat, mustard (*Brassica campestris*), sunflower) than in a fallow-based (rainy season fallow followed by other post rainy season crops) system and was in the order: groundnut–groundnut > groundnut–chickpea > groundnut–wheat > groundnut–mustard > groundnut–sunflower, though SYI was the highest in the groundnut–groundnut system in Vertisols (Typic Haplustert).

8.5.2 Relationships of SYI to SOC stock

A highly significant positive correlation is observed between SYI and SOC stock in groundnut ($R^2=0.93$, $P<0.001$), finger millet ($R^2=0.93$, $P<0.001$) in groundnut–finger millet rotation, finger millet monocropping ($R^2=0.90$, $P<0.01$), and sorghum ($R^2=0.81$, $P<0.01$), whereas these relationships are weak in groundnut monocropping, pearl millet, cluster bean, castor, safflower, rice, and lentil (Table 5.9). Manna et al. (2005) reported similar positive yield trends in the NPK and NPK + FYM treatments in soybean–wheat system on Alfisols at Ranchi, Bihar. Beneficial effect of application of organic materials as a source of N on sorghum grain yield has been reported earlier by Bellakki and Badanur (2000). But these relationships may not be always significant in case of soybean. Thus, the maintenance of SOC stock through application of FYM and chemical fertilizers is essential to the sustainability of rainfed production systems particularly in cropping systems like soybean–safflower that need high external inputs. Any improvement in SOC enhances available water capacity of

Table 5.9 Relationships of SYI to the carbon stock and magnitude of SOC sequestered after long-term cropping, fertilization, and manuring (Srinivasarao et al., 2011d, 2012a,b,c,d,e,f)

Parameters	SYI vs. carbon stocks	SYI vs. SOC sequestered
Anantapur (groundnut)	$SYI_{Groundnut}=0.008X+0.051$ ($R^2=0.48^{*}$)	$SYI_{Groundnut}=0.015X+0.30$ ($R^2=0.98^{***}$)
Bangalore (groundnut–finger millet rotation)	$SYI_{Groundnut}=0.01X-0.25$ (0.93^{***})	$SYI_{Groundnut}=0.01X+0.17$ (0.93^{***})
	$SYI_{Finger\ millet}=0.02X-1.02$ (0.97^{**})	$SYI_{Finger\ millet}=0.02X+0.57$ (0.97^{***})
Bangalore (finger millet)	$SYI_{Finger\ millet}=0.03X-1.53$ (0.90^{**})	$SYI_{Finger\ millet}=0.03X+0.29$ (0.90^{**})
Solapur (winter sorghum)	$SYI_{Sorghum}=0.004X+0.20$ (0.81^{*})	$SYI_{Sorghum}=0.004X+0.41$ (0.81^{*})
S.K. Nagar (pearl millet)	$SYI_{Pearl\ millet}=2.01X-0.07$ (0.61^{*})	$SYI_{Pearl\ millet}=0.02X+0.34$ (0.67^{*})
	$SYI_{Cluster\ bean}=5.99X-0.44$ (0.77^{**})	$SYI_{Cluster\ bean}=0.05X+0.84$ (0.77^{**})
	$SYI_{Castor}=1.64X+0.16$ (0.64^{*})	$SYI_{Castor}=0.01X+0.50$ (0.56^{*})
Indore (soybean)	$SYI_{Soybean}=-0.001X+0.51$ (0.03^{NS})	$SYI_{Soybean}=-0.001X+0.45$ (0.03^{NS})
	$SYI_{Safflower}=0.01X-0.19$ (0.63^{*})	$SYI_{Safflower}=0.008X+0.29$ (0.63^{*})
Varanasi (upland rice)	$SYI_{Rice}=0.01X+0.04$ (0.65^{*})	$SYI_{Rice}=0.01X+0.22$ (0.65^{*})
	$SYI_{Lentil}=0.01X-0.09$ (0.69^{*})	$SYI_{Lentil}=0.02X+0.19$ (0.69^{*})

*, **, *** denote significance at $P<0.05$, 0.01, and 0.001 respectively.

the soil profile (Du et al., 2009), which reduces frequency and intensity of the drought stress. Although the application of organics may not drastically increase the SYI of soybean, it can sustain the agronomic productivity of the soybean–safflower system on a long-term basis. Besides including a legume in sequence, combined use of available organic sources along with chemical fertilizers might prove beneficial for long-term productivity and sustainability of the system (Behera et al., 2007). A significantly higher SYI in soybean

has been obtained by the sole application of chemical fertilizers. This trend is mainly attributed to resilience of soil system to intermittent droughts with high WHC in plots receiving organic amendments compared with those receiving inorganic fertilizers in case of post rainy season crop of safflower. Such a positive response underlines the importance of organics in enhancing soil resilience under harsh climatic conditions during the cropping period, a common feature of rainfed agriculture. In comparison, soybean, being a nutrient (i.e., P) exhaustive crop, requires more nutrients during the growing period. Manna et al. (2005) reported negative yield trend of soybean with unbalanced use of N and NP application in a Vertisol.

8.5.3 Relationships of SYI to SOC sequestration

A highly significant positive correlation is observed between SYI and SOC sequestered (Table 5.9) in groundnut monocropping ($R^2=0.98$, $P<0.001$), groundnut ($R^2=0.93$, $P<0.001$), finger millet ($R^2=0.97$, $P<0.001$) in groundnut–finger millet rotation, finger millet monocropping ($R^2=0.90$, $P<0.01$), sorghum ($R^2=0.81$, $P<0.01$), and cluster bean ($R^2=0.77$, $P<0.01$). However, these relationships are relatively weak in crops like pearl millet, castor, safflower, rice, and lentil (Table 5.9).

8.5.4 Carbon inputs in diverse rainfed production systems

Component-wise C input (leaf, stubble, root, nodules, and rhizodeposition) as well as external inputs through FYM/GNS/CR/Leucaena GLM and cumulative C inputs into soil under different treatments during the long-term experiments are given in Figs. 5.16 and 5.17. In case of groundnut monocropping, the highest C inputs through CR (internal) are added in 50% RDF + 4 Mg ha^{-1} of GNS (1781 kg ha^{-1}), followed by 50% RDF + FYM 4 Mg ha^{-1} (1644 kg ha^{-1}) and the lowest is in control (505 kg ha^{-1}). Combining external C inputs through GNS or FYM, the total C inputs ranged between 505 kg ha^{-1} in control and 3461 kg ha^{-1} (50% RDF + 4 Mg ha^{-1} of GNS; Fig. 5.16A). The input of C from CR in soils under different treatment is also the highest in 50% RDF + 4 Mg ha^{-1} GNS (1981 kg ha^{-1}) followed by that in 50% RDF + FYM 4 Mg ha^{-1} (1644 kg ha^{-1}) (Srinivasarao et al., 2012a).

In case of finger millet monocropping, the highest mean annual C inputs through CR and FYM were added in FYM 10 Mg ha^{-1} + 100% NPK, followed by FYM 10 Mg ha^{-1} + 50% NPK, FYM 10 Mg ha^{-1} and the lowest was in control (Fig. 5.16B). Fertilization through balanced NPK or FYM or their combined use produced higher biomass and subsequently higher

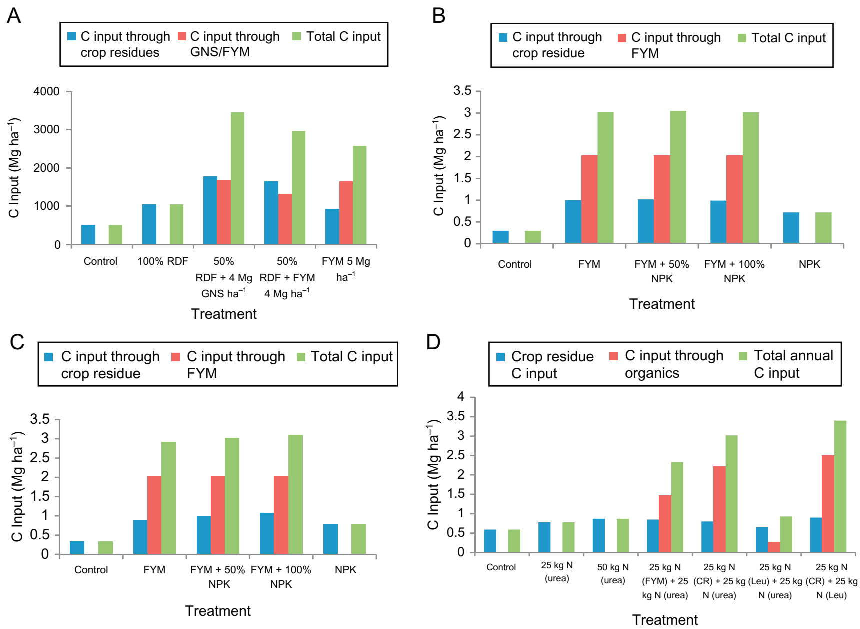

Figure 5.16 Annual C input to soil from rainfed (A) groundnut, (B) finger millet, (C) groundnut–finger millet rotation, (D) winter sorghum under different fertilizer and manure treatments.

C input in terms of CR (0.79–1.08 Mg C ha^{-1} $year^{-1}$) compared to control (Srinivasarao et al., 2012c). Similar trend is also observed in groundnut–finger millet rotation (Fig. 5.16C). In case of groundnut–finger millet rotation, the cumulative C input ranged from 3.9 Mg C ha^{-1} in the control to 39.6 Mg C ha^{-1} in the FYM + 50% NPK treatment (Fig. 5.16C). Fertilization through balanced NPK, FYM, or their combined use produced higher biomass and subsequently higher C input in terms of CR (0.72–1.02 Mg C ha^{-1} $year^{-1}$) compared to control. The treatments comprising FYM addition received the extra 2.03 Mg C ha^{-1} $year^{-1}$ (Srinivasarao et al., 2012b).

In case of winter sorghum, the cumulative C input ranged from 12.9 Mg C ha^{-1} in the control to 74.8 Mg C ha^{-1} in the 25 kg N (CR) + 25 kg N (*Leucaena*) treatment (Fig. 5.16D). Complementary use of organic materials along with fertilizer or application of equivalent amount of 50 kg N ha^{-1} completely through organic material (CR and *Leucaena*) produced higher biomass and subsequently higher C input in terms of CRs (0.9–3.4 Mg C ha^{-1} $year^{-1}$) compared with control (0.6 Mg C ha^{-1} $year^{-1}$)

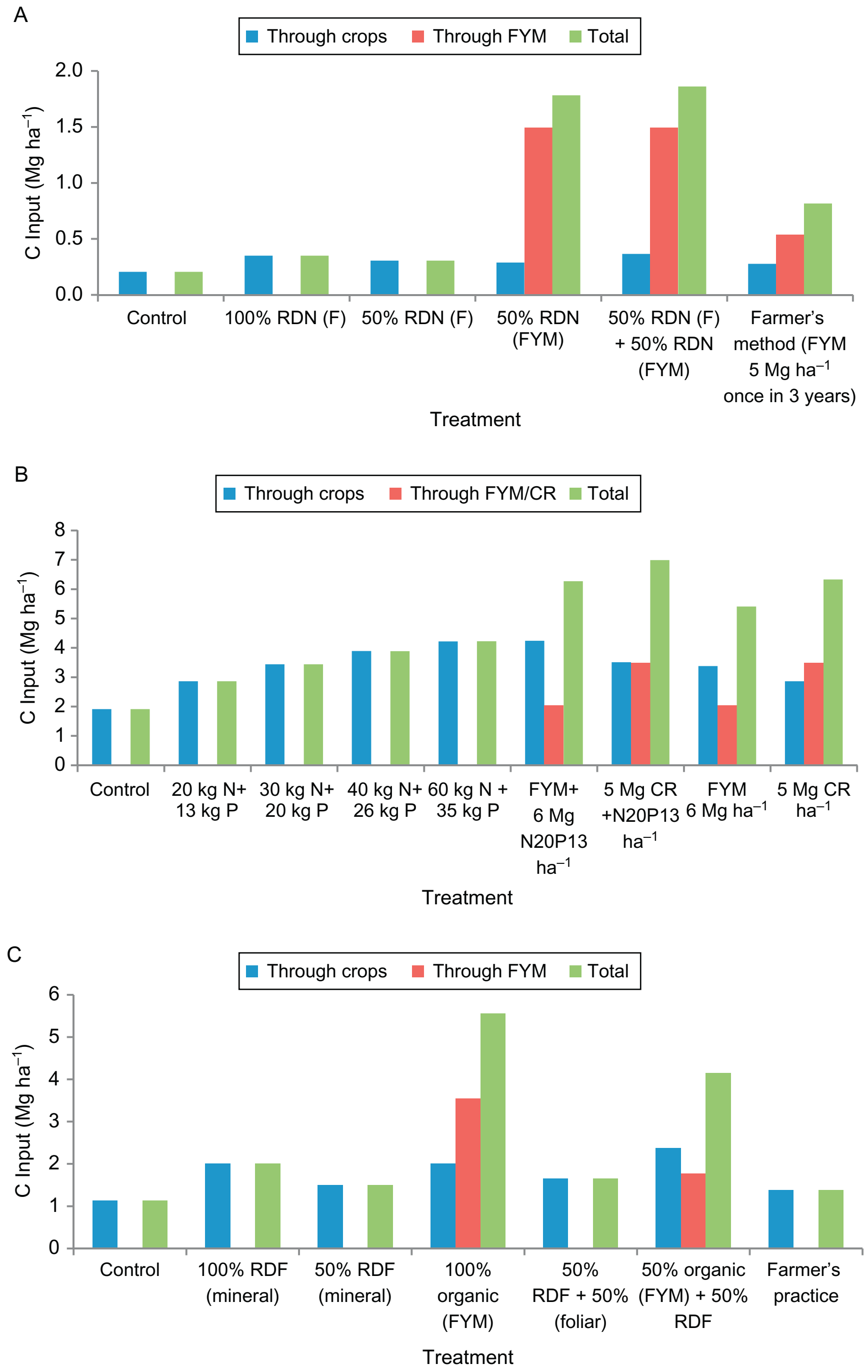

Figure 5.17 Annual C input to soil from rainfed (A) pearl millet–cluster bean–castor rotation, (B) soybean–safflower sequence, (C) rice–lentil sequence under different fertilizer and manure treatments.

and N application through chemical fertilizers (Srinivasarao et al., 2012d). Treatments comprising FYM/CR/*Leucaena* GLM addition received the extra 0.3–2.5 Mg C ha^{-1} $year^{-1}$ in the form of organic materials.

In case of pearl millet–cluster bean–castor, the highest C inputs through CR (internal) were measured in 50% RDN (fertilizer) + 50% RDN (FYM; 6.6 Mg ha^{-1}), followed by that in 100% RDN (fertilizer; 6.3 Mg ha^{-1}), and the lowest in control (3.7 Mg ha^{-1}; Fig. 5.17A). Combined with the external C inputs through FYM, total C inputs ranged between 3.7 Mg ha^{-1} in control and 33.5 Mg ha^{-1} in 50% RDN (fertilizer) + 50% RDN (FYM). The magnitude of C inputs through CR was in proportion to the nutrients applied (Srinivasarao et al., 2011d).

In case of soybean–safflower sequence, the cumulative C input ranged from 28.7 Mg C ha^{-1} in the control to 104.9 Mg C ha^{-1} in the 5 Mg CR + $N_{20}P_{13}$ ha^{-1} treatment (Fig. 5.17B). Application of nutrients supplied through either chemical fertilizers or organic material (CR and FYM), or by conjunctive use of organic materials along with fertilizer produced higher biomass and subsequently higher C input in terms of CR (2.86–4.24 Mg C ha^{-1} $year^{-1}$) compared with the control (1.91 Mg C ha^{-1} $year^{-1}$). Treatments comprising FYM/CR addition received the extra 2.03–3.48 Mg C ha^{-1} $year^{-1}$ in the form of organic materials (Srinivasarao et al., 2012e).

In case of rice–lentil sequence, inputs of C ranged from 1.1 Mg C $ha^{-1}$$year^{-1}$ in the control to 2.4 Mg C ha^{-1} $year^{-1}$ in the 50% organic (FYM) + 50% RDF treatment (Fig. 5.17C). Integrated use of FYM along with fertilizer produced higher biomass and subsequently higher C input, as CRs (2.4 Mg C ha^{-1} $year^{-1}$) compared with the 100% RDF treatment (2.0 Mg C ha^{-1} $year^{-1}$). Overall, treatments involving FYM received an additional 1.77–3.55 Mg C ha^{-1} $year^{-1}$ (Srinivasarao et al., 2012f).

8.5.5 Influence of root zone SOC stock on crop yield improvement

For every Mg ha^{-1} increase in SOC stock in the root zone, there was an increase in grain yield (kg ha^{-1}) of 13 for groundnut, 101 for finger millet, 90 for sorghum, 170 for pearl millet, 145 for soybean, 18 for lentil, and 160 for rice (Table 5.10). Thus, increasing SOC stock is essential to increasing productivity of rainfed crops in India and elsewhere in the tropics (Lal, 2010; Lal et al., 2003).

Table 5.10 Mean annual C input, C depletion rate, critical C input requirement, increase in crop yield (kg ha^{-1}) for every Mg ha^{-1}, increase in SOC stock in the root zone in different rainfed production systems (Srinivasarao et al., 2011d, 2012a,b,c,d,e,f)

Location/ production system	Mean annual C input (Mg C ha^{-1} year^{-1})	Mean C depletion rate (Mg C ha^{-1} year^{-1})	Critical C input requirement (Mg ha^{-1} year^{-1})	Yield increase (kg ha^{-1})
Anantapur (groundnut)	0.5–3.5	0.18	1.12	Groundnut: 13
Bangalore (groundnut–finger millet rotation)	0.3–3.0	0.92	1.62	Groundnut: 33 Finger millet: 124
Bangalore (finger millet)	0.3–3.1	0.25	1.13	Finger millet: 101
Solapur (winter sorghum)	0.6–3.4	0.23	1.10	Sorghum: 90
S.K. Nagar (pearl millet–cluster bean–castor)	0.2–1.9	0.67	3.30	Pearl millet: 170 Cluster bean: 140 Castor: 150
Indore (soybean–safflower)	1.9–7.0	0.47	3.47	Soybean: 145 Safflower: 59
Varanasi (upland rice–lentil)	1.1–5.6	0.15	2.47	Rice: 160 Lentil: 18

8.5.6 Profile SOC stock and SOC sequestration rate as influenced by nutrient management

Nutrient management, particularly application of organics, increased the profile SOC stocks compared to control. The highest SOC stock (Mg ha^{-1}) was measured in 50% RDF + 4 Mg ha^{-1} GNS (47.2) followed by that in 50% RDF + FYM 4 Mg ha^{-1} (45.9), FYM 5 Mg ha^{-1} (42.4), 100% RDF (36.2), and the lowest in the control (32.2) in groundnut-based system (Fig. 5.18A). In case of finger millet monocropping, the profile SOC stock (Mg ha^{-1}) was the highest in the FYM 10 Mg ha^{-1} + 100%

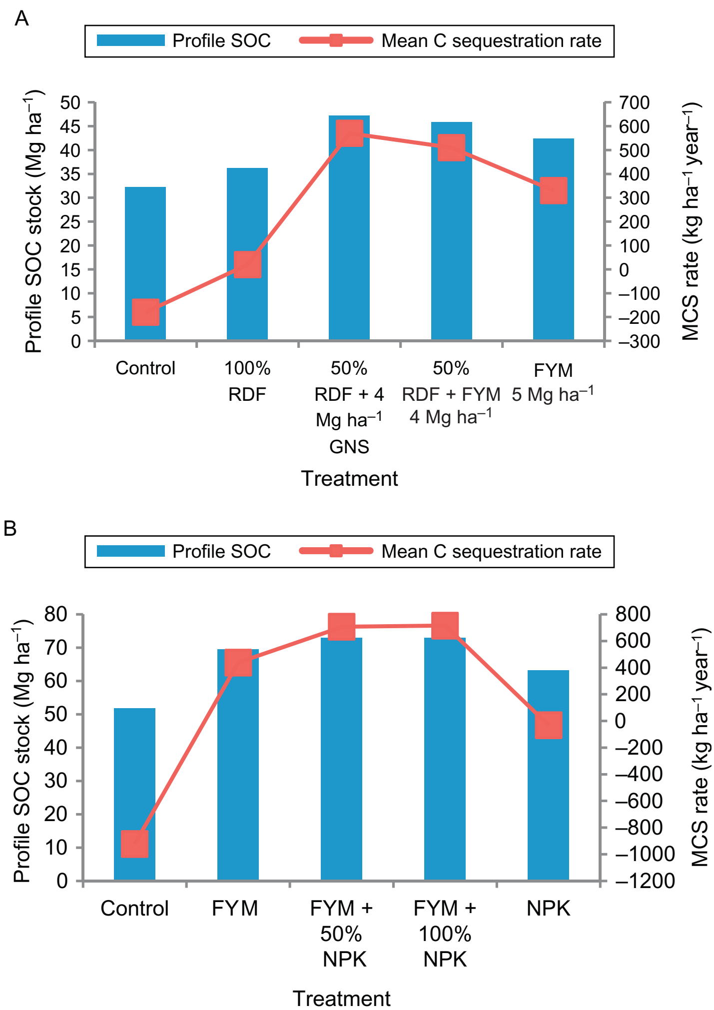

Figure 5.18 Profile SOC and mean C sequestration rate as affected by (A) 20 years of groundnut cropping and (B) 27 years of finger millet cropping with variable fertilization under semiarid tropical conditions.

NPK (85.7) followed by FYM 10 Mg ha^{-1} + 50% NPK (81.6) > FYM 10 Mg ha^{-1} (79.1) > NPK (70.5) and control (63.5) treatments (Fig. 5.18B). In case of groundnut–finger millet rotation, the SOC stock (Mg ha^{-1}) was the highest in the FYM + 100% NPK (73.0), and it was on par with FYM + 50% NPK (72.9)>FYM (69.4)>NPK (63.3)> control (51.7) treatments (Fig. 5.19A). In case of sorghum, the highest SOC stock

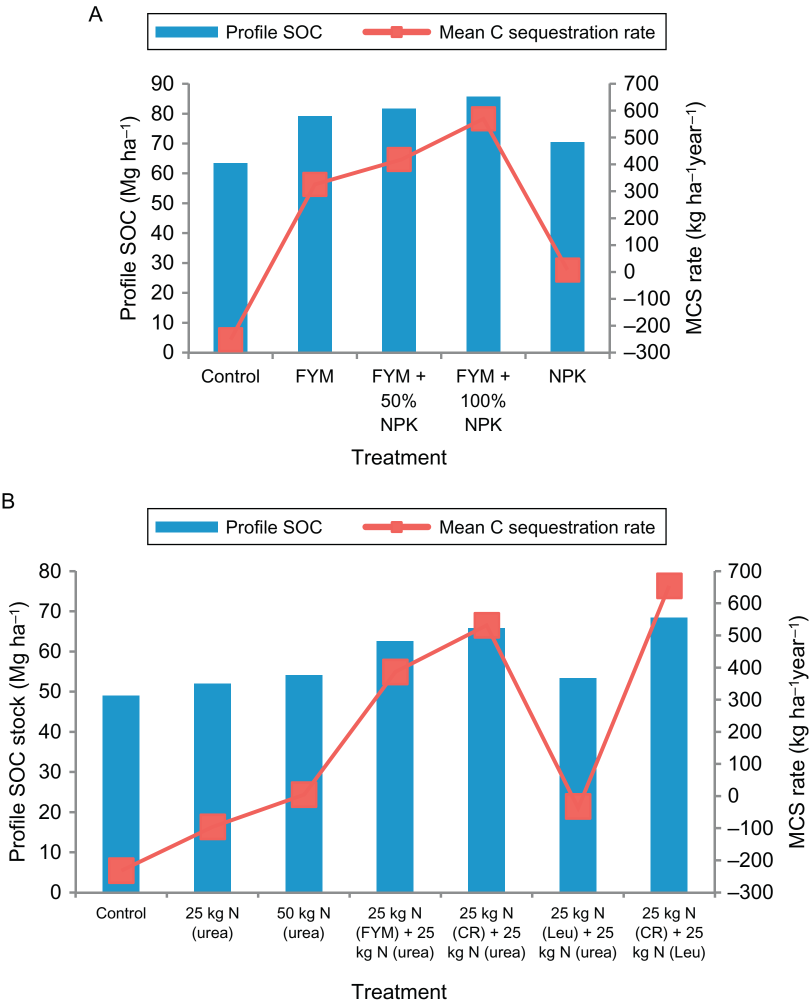

Figure 5.19 Profile SOC and mean C sequestration rate as affected by (A) 13 years of groundnut–finger millet rotation and (B) 22 years of sorghum cropping with differential manuring and fertilization under semiarid tropical conditions.

(Mg ha^{-1}) of 68.5 was observed in the 25 kg N (CR) + 25 kg N (*Leucaena*) followed by that of 65.8 in the 25 kg N (CR) + 25 kg N (urea) > that in the 25 kg N (FYM) + 25 kg N (urea) (62.6) > 50 kg N (urea) (54.1) = 25 kg N (*Leucaena*) + 25 kg N (urea) (53.4), and the lowest (49.0) in the control (Fig. 5.19B). In case of pearl millet-based system, the profile SOC stock

(Mg ha^{-1}) was the highest in 50% RDN (fertilizer) + 50% RDN (FYM; 25.5) followed by that in the 50% RDN (FYM) (23.4), and the lowest in the control (17.9) (Fig. 5.20A). In case of soybean–safflower sequence, the highest SOC stock (Mg ha^{-1}) of 69.9 was observed in the FYM 6 Mg + $N_{20}P_{13}$ ha^{-1} treatment followed by that of 68.7 in the 5 Mg CR + $N_{20}P_{13}$ ha^{-1} greater than that in the FYM 6 Mg ha^{-1} (66.0) > 5 Mg CR ha^{-1} (63.6) = 60 kg N + 35 kg P (62.7), and the lowest SOC stock (51.0) was found in the control (Fig. 5.20B). In case of rice–lentil sequence, the SOC stock (Mg ha^{-1}) was in the order 100% organic (FYM) (27.5) > 50% organic (FYM) + 50% RDF (24.0) > 100% RDF (mineral) (20.5) > 50% RDF + 50% (foliar) (19.2) = 50% RDF (mineral) (19.0) = farmer's practice (18.7) > control (17.8) (Fig. 5.20C).

Improved nutrient management practices were identified on the basis of the mean rate of SOC sequestration. The average SOC sequestration rate (kg C ha^{-1} $year^{-1}$) measured with different management treatments were: (1) 570 for 50% RDF + 4 Mg ha^{-1} GNS, (2) 570–720 for 10 Mg ha^{-1} FYM + 100% NPK, (3) 650 for 25 kg N ha^{-1} (sorghum residue) + 25 kg N (*Leucaena* clippings), (4) 240 for 50% RDN (fertilizer) + 50% RDN (FYM), (5) 790 for 6 Mg ha^{-1} FYM + 20 kg N + 13 kg P, and (6) 320 for 100% organic (FYM).

8.5.7 Minimal carbon input requirements for arresting C depletion

Long-term cropping without using any organic amendment and/or mineral fertilizers causes depletion of the SOC stock. This depletion ranges from 0.15 Mg C ha^{-1} $year^{-1}$ in rice-based system to 0.92 Mg C ha^{-1} $year^{-1}$ in groundnut–finger millet system (Table 5.10). The highest rate of depletion was observed in groundnut–finger millet system of 0.92 Mg C ha^{-1} $year^{-1}$ in semiarid Alfisols followed by 0.67 Mg C ha^{-1} $year^{-1}$ in pearl millet-based system in Entisols, and 0.47 Mg C ha^{-1} $year^{-1}$ in soybean-based system in Vertisols. The SOC depletion has been the least in rice-based system. There is a negative relationship between mean annual C inputs and mean SOC depletion rate across locations, soil types, and production systems (Fig. 5.21A). However, the mean annual rainfall plays a significant role in SOC depletion. Thus, a reciprocal relationship exists between rainfall amount and the SOC depletion rate (Fig. 5.21B). A similar long-term study assessed the SOC sequestration potential (CSP), defined as the rate of increase in the SOC stock over the antecedent stock in the 0–0.2 m depth. The CSP ranged from −0.178 Mg C $ha^{-1}$$year^{-1}$ (unfertilized control) to 0.572 Mg C ha^{-1} $year^{-1}$ (50% RDF + 4 Mg GNS ha^{-1}; Bhattacharyya

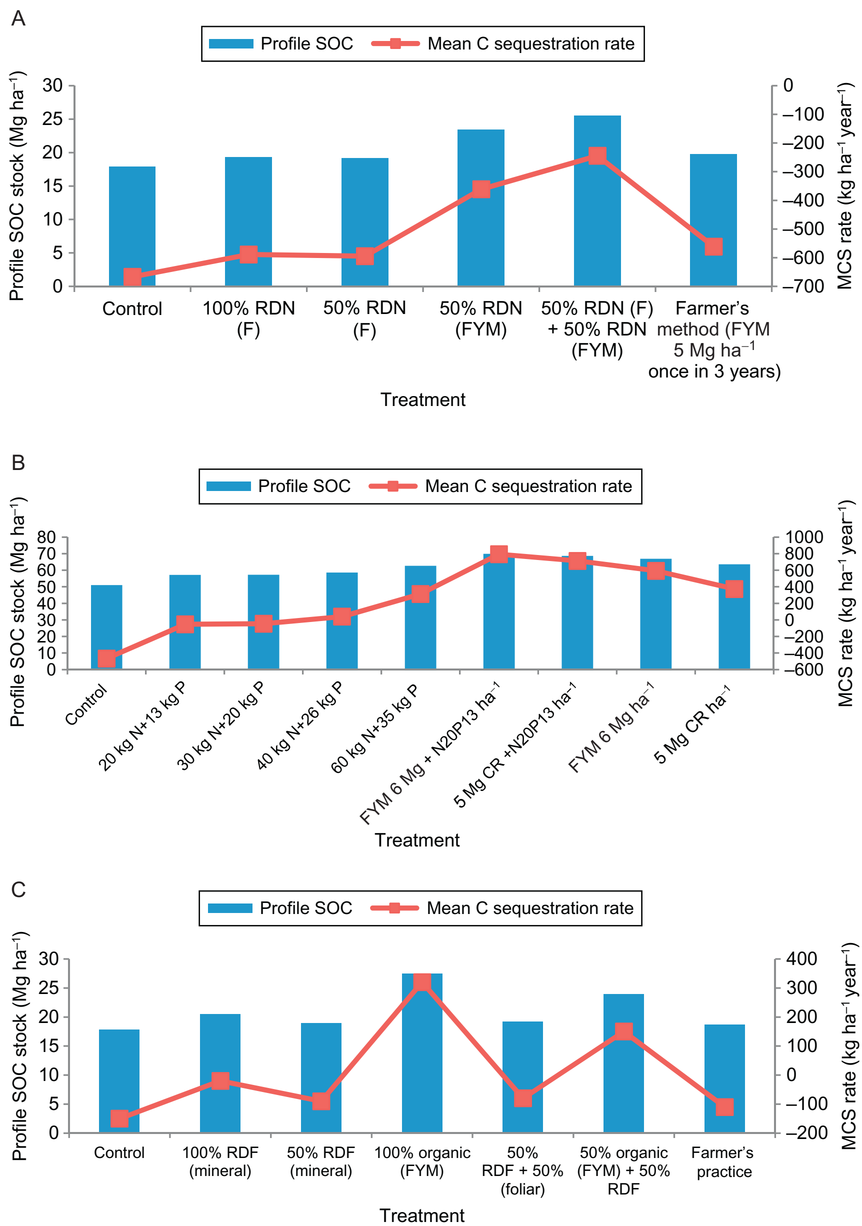

Figure 5.20 Profile SOC and mean C sequestration rate as affected by (A) 18 years of pearl millet cropping, (B) 15 years of soybean-cropping, and (C) 21 years of rice–lentil cropping with variable fertilization under arid tropical conditions.

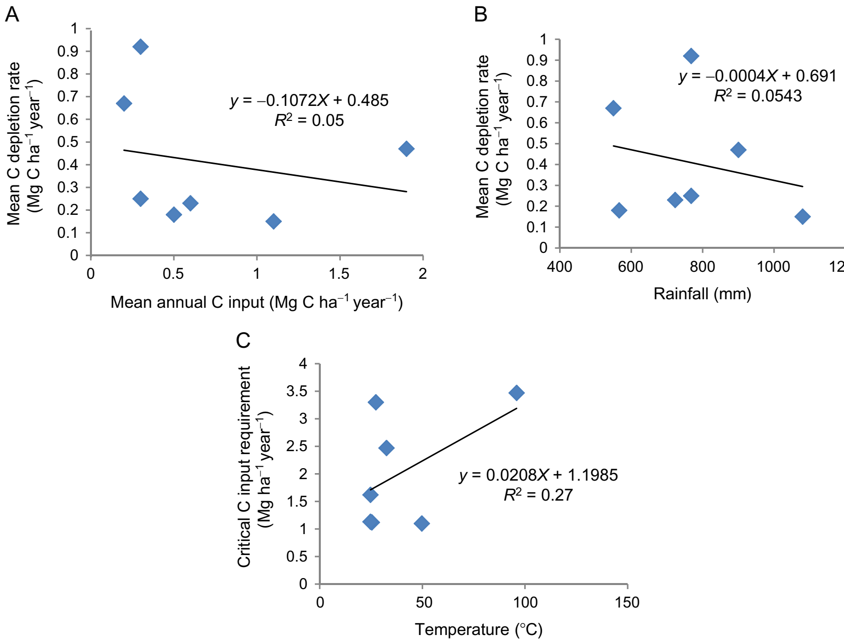

Figure 5.21 Relationship between (A) mean annual C inputs and mean C depletion rate (top left), (B) mean annual rainfall and mean C depletion rate (top right), and (C) critical C input requirement and mean temperature in seven long-term experiments in diverse rainfed regions of India.

et al., 2009). Globally, rates of C sequestration by different types of management range from 0.11 to 3.04 Mg C $ha^{-1}year^{-1}$, with a mean of 0.54 Mg C ha^{-1} $year^{-1}$, and are highly influenced by soil type and climate (Conant et al., 2001; West and Post, 2002). The positive linear relationship between the changes in SOC stock and the total cumulative C inputs to the soils (external organics plus CR) over the years has been highly significant and indicates that even after 13–27 years of C input, ranging from 0.2–1.9 Mg C $ha^{-1}year^{-1}$ in pearl millet-based system to 1.9–7.0 Mg C ha^{-1} $year^{-1}$ in soybean–safflower system, the unsaturated C sink capacity is not filled. Therefore, these soils have a high C sink capacity. However, sink capacity and/or sequestration rate cannot continue indefinitely (Six et al., 2002). Each soil with a different C loading may reach a new steady state of SOC stock over time. Assessment of SOC stock for these treatments at periodic, perhaps decadal, intervals may provide insights into the strategies of C management in these soils. Lal et al. (2007) estimated

that the rate of SOC sequestration in the United States, ranging from 100 to 1000 kg ha^{-1} year^{-1}, depends on climate, soil type, and site-specific management. The global potential of SOC sequestration and restoration of degraded/decertified soils is estimated at 0.6–1.2 Pg C year^{-1} for about 50 years with a cumulative sink capacity of 30–60 Pg (petagram = 10^{12} g = billion metric ton; Lal, 2004; Lal et al., 2007), comprising 0.4–0.8 Pg C year^{-1} through adoption of RMPs on cropland (1350 Mha), and 0.01–0.03 Pg C year^{-1} on irrigated soils (275 Mha), and 0.01–0.3 Pg C year^{-1} through improvements of rangelands and grasslands (3700 Mha). Maintaining a constant level of SOC stock (zero change) requires C input of 1.10 Mg C ha^{-1}year^{-1} in Vertisols under winter sorghum system to 3.47 Mg C ha^{-1}year^{-1} under a soybean-based system. The rate of C input required for groundnut, finger millet, and winter sorghum system is much lower than those reported by Kong et al. (2005) (3.1 Mg ha^{-1} year^{-1}) for Davis, California, USA and 4.59 Mg ha^{-1} year^{-1} by Majumder et al. (2007) for rice–wheat–jute system, 3.56 Mg ha^{-1} year^{-1} (Majumder et al., 2008) for irrigated rice–wheat systems of the Indo-Gangetic plains, and 2.92 Mg ha^{-1} year^{-1} by Mandal et al. (2007) for rice-based system in some soils of subtropical India. The lower input of C needed to maintain a constant level in this study may be due to lower initial SOC levels (1.4–3.9 g kg^{-1} soil; Srinivasarao et al., 2009b). In the studies referred to above, the initial SOC concentrations were approximately three to six times higher (>6–15 g kg^{-1} soil) than those in the present study. But in case of soybean, pearl millet, and upland rice, this rate is comparatively higher (Srinivasarao et al., 2011d, 2012e,f). In case of soybean–safflower sequence cultivated in Vertisols, initial SOC concentration of the soil was relatively high (6.2 g kg^{-1}). To maintain or improve upon this level, a substantial input of biomass C is required. In case of pearl millet-based system in Entisol, soil was degraded and had low inherent fertility. Summer temperatures of the experimental sites are also high compared to other locations, which may be the reason for requirement of higher critical C input. Thus, a positive relationship has been observed between temperature and critical C input requirement (Fig. 5.21C), indicating the need of a higher or repeated C inputs to maintain SOC in tropical dry ecosystems. Information regarding critical C input requirement for maintaining SOC stock at antecedent level for specific locations is strategically an important information in terms of C sequestration, soil quality management, and advancing food security in semiarid regions (Lal, 2004; Mandal et al., 2007).

8.6. Constraints to enhancing soil carbon stocks in drylands

Both the magnitude and the quality of SOC stock are critical to improving soil quality, increasing crop productivity, and offsetting CO_2 emissions (Lal, 2004; Smith, 2007). Optimum levels of SOC can be achieved through the adoption of appropriate crop rotations (Wright and Hons, 2005), fertility management by using a combination of inorganic fertilizers and organic amendments (Majumder et al., 2008; Mandal et al., 2007; Schuman et al., 2002), and conservation tillage methods (Lal, 2009). In rainfall-scarce environments of tropical and subtropical regions characterized by arid and semi-arid climates, soils are inherently low in SOC stock, and food security is strongly related to soil quality. Therefore, curtailing depletion and enriching SOC stock are essential to adapting to and mitigating of the climate change, buffering agroecosystems in harsh climates against extreme events (drought), and stabilizing agronomic productivity by ensuring some returns even during the drought-prone seasons. In these harsh environments, the minimum assured yield even during the bad seasons is more important than the high yields only during the good seasons.

Crop cultivation adversely affects the distribution and stability of soil aggregates and reduces SOC stock (Kong et al., 2005). The magnitude of reduction in SOC stock due to cropping, however, varies among climates and cropping systems (Lal, 2004). Because of the prevailing high temperatures, soils of tropics generally emit more oxidative products (i.e., CO_2) per unit SOC stock than those of temperate and cooler regions. However, crop species also play an important role in maintaining quantity and quality of SOC stock despite diverse nature of CRs with highly variable turnover or residence time in the soil (Mandal et al., 2007).

The duration and timing of "fallowing" within a cropping system can also affect the magnitude of SOC stock (Halvorson et al., 2002) because of the differences in cropping intensity and specific management practices. Most of the research done thus far on SOC sequestration in soils of agroecosystems is confined to cold and temperate regions. The effects of soil moisture regime on SOC decomposition (and hence, long-term SOC storage) are highly variable.

Most soils of rainfed regions are characterized by low SOC and N stocks despite large variations in the cropping system, soil type, rainfall, temperature, and supplementary management practices such as manuring and fertilization. Low crop yields, low or no biomass residue retention, coupled with long fallow periods that extend up to 9 months in a year result in harsh environments that do not sustain high levels of SOC stocks. However, the

magnitude of decline or enhancement of SOC due to continuous cultivation depends on the balance between the loss by oxidative forces during tillage, the quantity and quality of CRs that are returned, and the organics added to the soils. Therefore, crop and soil management practices have to be adapted to ensure long-term sustainability. The use of inorganic fertilizers, organic amendments, and the inclusion and cultivation of legumes enhance SOC stock and its sustainability.

8.7. Limitations of nutrients and water in enhancing soil carbon stocks

SOM has a significant effect on agronomic productivity. However, due to numerous constraints, the rate of application of organic manures and CR to arable land has declined in the country over time. Throughout the dry ecosystems in India, the common source of organic residues retained in the soil to contribute to SOC stock is through input of roots. However, low biomass production in this region due to drought stress and nutrient deficiency in soils results in low input of even the root biomass. Given the ever exacerbating nutrient imbalance, even if the entire amount of organic manures produced in the country is applied to arable land, it will not suffice to alleviate the nutrient deficiency in the soil system. Study of the predominant physical and chemical properties of 21 profiles indicated that most soils are low in SOC with concentration of <0.5%. Low SOC concentration in these soils is one of the important factors contributing to low soil fertility. With a few exceptions, most soils are also low in available N, available P ranges from low to high, and available K and S from low to high. Available Zn is below the critical level in Rajkot, Anantapur, Rewa, Akola, Bellary, Bijapur, and Solapur, Agra, S.K. Nagar, Arjia, Hoshiarpur, and Rakh Dhiansar. Soil concentration of Fe is deficient in Rajkot, Bellary, and Bijapur. Surface layers of several profiles are deficient in available Ca (<1.5 cmol(+) 100 g^{-1}) such as in Phulbani, Anantapur, S.K. Nagar, and Bangalore. Surface layers of soils at Phulbani, Ranchi, Anantapur, Agra, Hisar, S.K. Nagar, Bangalore, Arjia, Hoshiarpur, and Rakh Dhiansar are deficient in Mg (<1.0 meq(+) 100 g^{-1}). Of the 21 locations, 11 are deficient in B. Except Indore, all other soils are multinutrient deficient. Due to sloping terrain in dry ecosystem, a large proportion of rainfall is lost as runoff, along with the nutrient- and SOC-rich surface layer. Nonetheless, adoption of watershed programs in site-specific soil and climatic conditions can reduce the runoff (30–35%) and soil losses (15–30%) (Table 5.6; Venkateswarlu et al., 2012).

9. BIOMASS INPUT INTO SOILS AND COMPETING USES OF CROP RESIDUES (CRs)

Most CR converted into high-value manure of better quality than FYM, and its use, along with chemical fertilizers, can help sustain or even increase the agronomic yield. Use of chemical fertilizers has played a significant role in intensification of cropping systems, along with a strong increase in crop production. However, the increased use of inorganic fertilizers alone, often in an unbalanced manner, leads to decline in soil quality and multiple nutrient deficiencies even in regions of the high agronomic potential. Efficient CR management can also play a vital role in refurbishing soil productivity as well as in increasing the use efficiency of inorganic fertilizers. Thus, CR management is receiving a great deal of attention because of its diverse and positive effects on soil physical, chemical, and biological properties. Indeed, CR is a precious resource and must not be labeled as waste.

9.1. Availability of CRs

Ministry of New and Renewable Energy, of the Government of India (MNRE, 2009; www.nicra.iari.res.in/Data/FinalCRM.doc), has estimated that about 500 Tg of CRs are produced every year. There is a large variability in production of CR, and their use depends on the crops grown, cropping intensity, and productivity in different regions of India. Production of CR is the highest in Uttar Pradesh (60 Tg) followed by that in Punjab (51 Tg) and Maharashtra (46 Tg). Among different crops, cereals generate 352 Tg of residues followed by fibers (66 Tg), oilseed (29 Tg), pulses (13 Tg), and sugarcane (12 Tg). The cereal crops (rice, wheat, maize, millets) contribute 70% of the total CR comprising 34% by rice, 22% by wheat, and 13% by fiber crops. Among fibers, cotton generates the maximum amount (53 Tg) with 11% of total CR production. Coconut (*Cocos nucifera*) ranks second among fiber crops with 12 Tg of CR production. Sugarcane CRs, comprising tops and leaves, generate 12 Tg or 2% of total CR produced in India.

The surplus CRs (i.e., total residues produced minus the amount used for various purposes) are typically burned on-farm. The amount of surplus CR available in India is estimated between 84 and 141 Tg year^{-1} where cereals and fiber crops contribute 58% and 23%, respectively. The remainder CR of 19% is contributed from sugarcane, pulses, oilseeds, and other crops. Of the 82 Tg of surplus CR from the cereal crops, 44 Tg is from rice followed by

Figure 5.22 Cotton, maize, and combined harvested rice straw burning in Nalgonda, Kurnool, and Srikakulam rainfed districts of Andhra Pradesh. *Source: Srinivasarao et al. (2013).*

24.5 Tg from wheat, which is mostly burned on-farm. In case of fiber crops (33 Tg of surplus CR), approximately 80% is from cotton and is burnt on-farm (Fig. 5.22).

Use of CR has always been an important component of sustainable agriculture. Until the advent of inorganic fertilizers and mechanization, CRs were an integral part of farming as feed for livestock and litter for the production of FYM, which has been essential to the maintenance of soil fertility and sustainability of crop production (Srinivasarao et al., 2011a). In fact, CRs are still important to small-scale and subsistence farmers, and their importance in improving soil quality is growing because of the ever-decreasing access to free grazing land and expansion of cropland area. With increase in price of fertilizers, there will be an increasing emphasis on efficient use of CR both for meeting the nutrient requirements and SOC sequestration. Nutrient concentrations of different sources of CR (Tables 5.11 and 5.12) indicate their potential of nutrient supplying capacity. As most of the rainfed croplands are already multinutrient deficient (Table 5.13), recycling rather than burning of CR must be promoted to supplement the nutrients applied as chemical fertilizers.

9.2. Competing uses of CRs

Although benefits of CR incorporation are widely documented, the major problem is their availability. Most CRs (except the root biomass) are taken away in regions of rainfed farming. Above all, other farming practices (e.g., excessive tillage, harvesting of residues as animal feed, burning to facilitate preparation of a clean seed bed, open grazing) exacerbate the process of soil degradation and depletion of SOC and plant nutrients.

Table 5.11 NPK content (kg Mg^{-1}) of some organic manures and crop residues of some rainfed crops

Manure/residue	N	P_2O_5	K_2O	Total
Manures				
Cattle/buffalo dung	5.0	2.0	5.0	12.0
Sheep/goat dung	6.5	5.0	3.0	11.8
Pig dung	6.0	5.0	4.0	15.0
Poultry manure	18.0	23.0	14.0	55.0
Farmyard manure	7.8	7.2	6.5	21.5
Biogas slurry	14.0	9.2	8.4	31.6
Vermicompost	18.0	20.0	8.0	46.0
Crop residues				
Rice	6.1	1.8	13.8	21.7
Wheat	4.8	1.6	11.8	18.2
Sorghum	5.2	2.3	13.4	20.9
Maize	5.2	1.8	13.5	20.5
Pearl millet	4.5	1.6	11.4	17.5
Pulses	12.9	3.6	16.4	32.9
Oilseeds	8.0	2.1	9.3	19.4
Groundnut	16.0	2.3	13.7	32.0
Sugarcane	4.0	1.8	12.8	18.6

Source: Srinivasarao et al. (2011a)

Most CRs are widely used in India as animal feed, and this practice must be taken into account when assessing availability and profitability of livestock production systems. In addition to feed, CRs are also used as litter and bedding (providing FYM or compost), and chopped straw is also used as poultry litter. Among industrial uses, rice straw is a raw material for paper production, and as packing materials. Rice husk is widely used in semi-artisan brick manufacture; chopped straw mixed with mud is used for plastering, both internally and (in hot, dry climates) externally. Relatively strong stems of maize, sorghum and bulrush, or pearl millet are used in traditional building, screens, and in constructing traditional grain storage bins. Furthermore, long straw is used as thatch, and residues are widely used as fuel in rural communities and are often mixed into dung cakes for generating household energy (Fig. 5.23).

Table 5.12 Nutrient content of legume residue in comparison with cereal residue

	Crop residue		
	Cereal		Pulse
Nutrient content	Rice	Wheat	Lentil
C (%)	47.7	52.8	48
N (%)	0.54	0.64	1.64
P (%)	0.11	0.14	0.12
K (%)	1.68	0.94	1.68
Ca (%)	0.8	0.8	2
Mg (%)	0.48	0.24	0.24
S (%)	0.09	0.13	0.47
Zn (mg kg^{-1})	119	123	148
C:N ratio	88	85	29

Source: Srinivasarao et al. (2011a)

Table 5.13 Nutrient deficiencies in 1962 farmers' fields in eight rainfed districts of Andhra Pradesh

District	OC	N	P	K	S	Zn	B	Fe	Cu
Adilabad (139)*	L–M	L	L	H	D–S	D–S	D–S	S	S
Nalgonda (420)	L–M	L	L–H	L–M	D–S	D	D	D–S	S
Khammam (161)	L–M	L	L–H	L–H	D–S	D	D	S	S
Mahbubnagar (121)	L–M	L	L–M	M–H	D–S	D–S	D–S	S	S
Anantapur (340)	L	L	M–H	L–H	D	D–S	S–D	S	S
Kadapa (320)	L	L	L–M	L	D	D	D	D–S	D–S
Warangal (336)	L–M	L	M–H	L–M	D–S	D	D	S	S
Rangareddy (125)	L–M	L	L–M	L–H	D–S	D–S	D–S	S	S

*Number of farmers fields tested.
L, low; M, medium; H, high; D, deficient; S, sufficient.
Source: Srinivasarao et al. (2011a)

Despite their multiple and competing uses, CRs must be integral components of sustainable rainfed agriculture. Among options available to farmers for the management of CR (including burning), important are baling and removal, incorporation in the soil with tillage, and retention on the surface as mulch. Burning, while exacerbating the loss of organic matter and

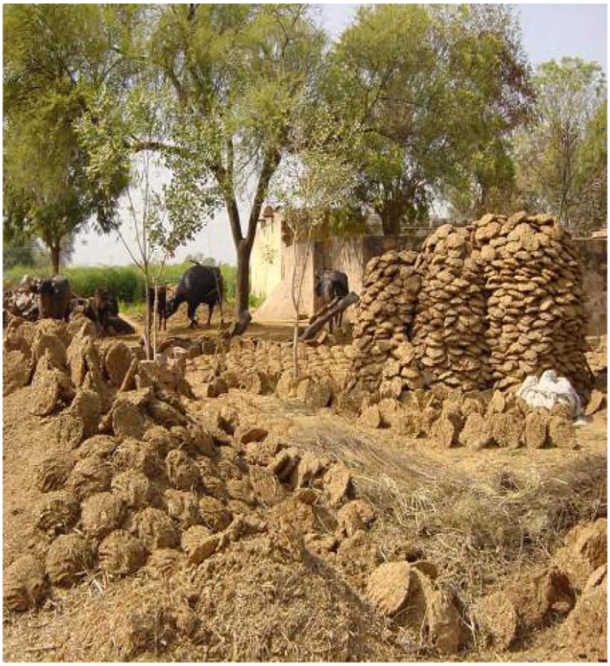

Figure 5.23 Cow dung as firewood cakes in some regions of India.

volatilization of nutrients along with adverse effects on soil biota, also causes air pollution and associated ill effects on human and animal health. In India, baling is not practiced by small land holders. Nonetheless, removal of CR by any means is a loss of organic resource essential to soil quality. However, it is also necessary to feed livestock and sustain the mixed farming. While soil incorporation of CR is beneficial in recycling nutrients, plowing under requires energy and time, leads to temporary immobilization of nutrients (e.g., N), and the C:N ratio needs to be corrected by applying N at the time of residue incorporation.

10. IMPROVED CROPPING SYSTEMS

Management strategies that maintain or enhance SOC stock have the potential of improving soil resources. Leguminous crops (e.g., pulses) add significant amount of organic matter to the soil through leaf drop and root biomass. Hence, the need to reduce both the on-site and off-site impacts of cereal-based rotation is an important reason for introducing pulses into rain-fed cropping systems.

10.1. Soil chemical properties

Both concentration and composition of organic matter input are important to soil quality. Despite the availability of voluminous literature, several questions of practical importance remain. The amount of below-ground biomass left in the soil depends on the species, soil type, and the degree of open grazing. Increasing SOC concentration of cultivated soils is a major challenge, particularly in dryland agriculture, unless legume or hay crops are included in the rotations, or organic matter is added from external sources.

Pulses are generally grown in neutral to alkaline soils. Pulse crops have the ability to reduce soil pH in the rhizosphere and make the microenvironment favorable to nutrient availability. The availability of nutrients in the fields cropped with pulses increases after their harvest and their residual effects is widely observed in the following crops (Ali et al., 2002). Further, pulses leave substantial amounts of N in the soil after their harvest (Srinivasarao et al., 2003). An improvement in the N budget of soils measured by improved soil reserves of readily mineralizable organic N and microbial biomass C and N are widely reported (Singh et al., 1999). Increased N availability is considered one of the important factors responsible for the beneficial effects of pulses on the following nonlegume crops (Ali et al., 2002).

10.2. Conservation agriculture in rainfed agroecosystems

Adoption of conservation agriculture (CA) in rainfed farming is an emerging dimension for recycling biomass into soil system and improving SOC stock in the surface layer. In arid (<500-mm rainfall) region, low tillage is comparable to CT and weed problem is manageable. In semiarid region (500–1000 mm), CT can be superior to reduced tillage, and successful crop production depends on water infiltration and conserving soil moisture in the profile. Weed infestation is an ephemeral problem depending upon the seasonal rainfall distribution in subhumid (~1000 mm of rainfall per annum) regions, but there is a possibility of reducing the intensity of CT by using herbicides. A long-term study comprising tillage (conventional (CT) and reduced (RT)) and conjunctive nutrient use (fertilizers and low cost farm-based organics) treatments conducted in Alfisol (Typic Haplustalf) at Hyderabad, India, involving sorghum and mung bean cropping system, indicated significant improvements in grain yields and SYI of several crops (Sharma et al., 2004). The results of this and

other experiments have raised the expectations of improving rainfed farming on Alfisols by using some kind of CA system. These soils are shallow, with compacted subsoil horizon (murrum layer), and are also susceptible to hard setting. To harness advantages of CA systems in semiarid tropics, it is essential to retain CR on the surface as mulch (Lal, 1997), which is a major challenge in India due to competing demands as fodder for livestock and other uses. But the potential for CA exists in rainfed crops like maize, pigeon pea, castor, cotton, sunflower, etc., where CRs are not used as feed and for other competing purposes. Soils cultivated for rainfed farming are prone to numerous constraints (e.g., surface sealing, cracking, and hard setting). Ensuring good seed germination and crop stand establishment are major challenges to be addressed with CA and CR management. Being the only source of water, interactions between rainwater conservation and CA must be studied in an integrated manner. With canopy cover of maize grown during the rainy season, there is a possibility of growing a postrainy legume (i.e., horse gram or *Macrotyloma uniflorum*) crop in degraded Alfisols of Southern India, which is otherwise a monocropped area (Fig. 5.24).

10.3. Pulse residue: A rich source of nutrients

The C:N ratio and concentration of other nutrients in CR of pulses is relatively high. Nutrient concentration of lentil residues indicates that N concentration is almost threefold higher than that in cereal residues (i.e., rice, wheat). Similarly, higher concentrations of Ca, S, and K are also reported in pulse residues (Table 5.12), which are recycled upon incorporation into the soil.

Figure 5.24 Possibility of second crop horse gram in post rainy season with maize crop (rainy season) residue cover in conservation agriculture (CA) experiment in monocropped dry ecosystem at Hyderabad, India.

Optimal soil conditions (e.g., moisture and temperature regimes, pH, salinity/sodicity, calcareousness, SOC concentration, and stock) are of rare occurrence under rainfed conditions. Although N availability can be somewhat improved by growing pulses and including leguminous crops in the rotation, most crops including legumes are prone to N deficiency. Further, legumes with deeper root system (e.g., pigeon pea) can explore nutrients from deeper layers of the profiles and recycle to the surface layer through leaf litter. Chickpea, through release of several organic acids in the rhizosphere, can mobilize soil nutrients, particularly P. These crops add C to soil in the form of rhizodeposition also. Legume residues also provide large amounts of N, P, K, Ca, Mg, S, Zn, and all other required nutrients besides biomass C (Table 5.12). The C:N ratio of legume residues is narrower than those of cereal residues.

10.4. Inclusion of legumes in the cropping systems: A strategy toward INM

By improving physical, chemical, and biological properties of soils, cultivation of food legumes can reverse the declining trend in productivity of cereal–cereal systems. Adoption of legume-based improved management systems can increase productivity besides maintaining better soil quality than that with the traditional system. But the amount of N fixed by these legumes varies widely (3–100 kg ha^{-1}) depending upon soil conditions.

11. CARBON SEQUESTRATION AND CLIMATE CHANGE

Soil C sequestration is an important strategy and is a win–win option of producing more food per unit area besides mitigation of climate change (Lal, 2004). Although soils of the tropical regions have low C sequestration rate because of high temperatures, adoption of appropriate management practices can lead to higher rates particularly in high rainfall regions (Srinivasarao et al., 2012f). The ecosystem C pool of cropping systems has two related but distinct components: soil C and vegetation C. Tree-based systems can sequester substantial quantities of C into biomass in a short period. Total potential of soil C sequestration in India is 39–49 Tg year^{-1} (Lal, 1997). This is inclusive of the potential of the restoration of degraded soils and ecosystems, which is estimated at 7–10 Tg C year^{-1} (Table 5.14). The potential of adoption of RMPs on agricultural soils can lead to sequestration of an additional 6–7 Tg C year^{-1}. In addition, there is also a potential of SIC sequestration estimated at 21.8–25.6 Tg C year^{-1}. A range of natural

Table 5.14 Soil organic carbon sequestration potential through restoration of degraded soils

Degradation process	Area (Mha)	SOC sequestration rate (kg $ha^{-1}year^{-1}$)	Total SOC sequestration potential (Tg C $year^{-1}$)
Water erosion	32.8	80–120	2.62–3.94
Wind erosion	10.8	40–60	0.43–0.65
Soil fertility decline	29.4	120–150	3.53–4.41
Water logging	3.1	40–60	0.12–0.19
Salinization	4.1	120–150	0.49–0.62
Lowering of water table	0.2	40–60	0.01–0.012
Total			7.20–9.82

Source: Lal (1997)

resource management strategies that reverse the degradation process have a large potential of C sequestration in India.

12. POLICY INTERVENTIONS

Incentivization is needed to motivate small land holders toward adoption of RMPs. Relevant policy interventions are needed to achieve the following:

- Improving soil quality through enhancing C sequestration because of its long-term implication to food security and climate change adaptation and mitigation.
- Strengthening dialogue between researchers and policy makers to identify policy interventions and land managers to identify demand driven R&D priorities.
- Establishing dedicated cells at the state-level institutions for adoption and impact assessment of suitable programs.
- Implementing suitable policy supports (e.g., nutrient-based subsidy or NBS) for ensuring balanced use of fertilizers, subsidy on use of organic manures, adequate extension support for increasing awareness among the farmers about the need for soil quality management and C sequestration, campaign against residue burning, and encouraging the farmers to retain the CRs that do not have any alternate uses, better mechanization for spreading the residues, etc.

- Promoting RMPs based on locally available organic resources as win–win options of improving productivity and SOC sequestration for advancing food security and improving the environment.
- Creating mechanisms of payments for ecosystem services through widespread adoption of RMPs.
- Strengthening the capacity of local institutions (e.g., self-help groups, banks, and agricultural credit societies) to promote efficient utilization of CRs, banning of residue burring, growing leguminous cover crops during off-season and its incorporation, large-scale promotion of green manuring like *Sesbania*, green leaf manuring like (e.g., *Gliricidia*, *Tefrotia*) on field bund at village/block level.
- Establishing public–private partnership in promoting investments on infrastructure, markets, and supply of inputs.
- Providing support to farmers for adopting RMPs in the form of *additional labor costs* and *seed material*.
- Investing on regeneration of biomass within and nearer to the agriculture areas to reduce costs of harvesting and transport, and providing logistic support for labor costs, planting material, and plant protection.
- Building human resource capacity through advanced training for researchers, extension agents, and farmers. Establishing self-help groups and encouraging unemployed youth to take up custom hiring of CA machineries as profession.

13. CONCLUSIONS

Poor soil quality with multiple nutrient deficiencies, low NUE, declining partial factor productivity are among major concerns in semiarid and rainfed agriculture. The SOC stock plays a crucial role in the soil quality, availability of plant nutrients, environmental functions, and the global C cycle. Soils of drylands are generally low in inherent fertility, low in SOM concentration, and hence have a high C sink capacity. Increasing C storage in the soil profile not only improves fertility but also abates global warming. Several factors related to soil type, production, and management influence C sequestration, and it is important to identify production and management factors that enhance C sequestrations in dryland soils. The SOC stocks in the soil profiles across the country show wide variations and follow the order: Vertisols > Inceptisols > Alfisols > Aridisols. Both SIC and TCSs are larger in Vertisols than in other soil types. The SOC stocks decrease with depth in the profile, while SIC stocks increase with depth.

Among the production systems, soybean, maize, and groundnut-based systems maintain higher SOC stocks than other production systems. Data from experiments involving long-term cropping, fertilization, and manuring show that mineral fertilizer application alone can neither sustain the productivity nor maintain the SOC stock. A strong depletion of C occurs irrespective of production systems and soil type. Application of organics along with mineral fertilizer can sustain productivity and sequester significant amount of soil C. The rate of depletion of SOC can range from 0.15 Mg C ha^{-1} $year^{-1}$ in rice-based system to 0.92 Mg C ha^{-1} $year^{-1}$ in groundnut–finger millet system. To arrest this, depletion C input of 1.10–3.47 Mg C ha^{-1} $year^{-1}$ is required as a maintenance dose. Further, potential of tropical soils to sequester more C in soil can be harnessed by identifying appropriate production systems and management practices for sustainable development and improved livelihoods in the tropics:

- The average SOC sequestration rate (kg C ha^{-1} $year^{-1}$) measured for different management treatments were: (1) 570 for 50% RDF + 4 Mg ha^{-1} GNS, (2) 570–720 for 10 Mg ha^{-1} FYM + 100% NPK, (3) 650 for 25 kg N ha^{-1} (sorghum residue) + 25 kg N (*Leucaena* clippings), (4) 240 for 50% RDN (fertilizer) + 50% RDN (FYM), (5) 790 for 6 Mg ha^{-1} FYM + 20 kg N + 13 kg P_2O_5, and (6) 320 for 100% organic (FYM).
- For every one Mg ha^{-1} increase in SOC stock in the root zone, there was an increase in grain yield (kg ha^{-1}) of 13 for groundnut, 101 for finger millet, 90 for sorghum, 170 for pearl millet, 145 for soybean, 18 for lentil, and 160 for rice.
- The critical level of C input requirements for maintaining SOC at the antecedent level ranged from 1 to 3.5 Mg C ha^{-1} $year^{-1}$ and differed among soil type and production system. It was 1.12, 1.62, 1.13, 1.10, 3.30, 3.47, and 2.47 Mg ha^{-1} $year^{-1}$ for groundnut, groundnut–finger millet rotation, finger millet, winter sorghum, pearl millet, soybean, and rice-based systems, respectively.

14. FUTURE RESEARCH NEEDS

Synthesis of the literature and the research data from long-term experiments conducted throughout the rainfed agriculture in India indicate the following researchable priorities:

- Compiling inventory of region-specific CRs including total production from different crops, their quality, utilization, and amount burned on-farm for developing management strategies. Satellite imageries can be used to estimate the amount of residues burned on-farm.
- Establishing new and continuation of the existing long-term (>10 years) field experiments to quantify the influence of RMPs on the soil C sequestration in diverse ecosystems and crop production systems, GHG emissions, and ecosystem services.
- Conducting life cycle analyses of residue-based CA vis-à-vis burning and other scenarios of CRs management. The strategy is to develop management options to alleviate constraints and successfully adapt CA under diverse soils and ecoregions by analyzing the benefit:cost ratio, socio-economic and technical feasibility of off- and on-farm use of CRs. Where CRs have competing uses as fodder or fuel, systems must be developed to facilitate recycling of the end product (dung, slurry, ash) in conjunction with CA.
- Optimizing the use of CRs in conjunction with CA without affecting the crop-livestock system, particularly for the regions where residues are the main source of fodder. The CA systems can be adopted to crops whose residues are not used as fodder.
- Strengthening the database on critical C input is required for maintaining and enhancing the SOC stock for diverse cropping systems, soil types, and ecoregions.
- Establishing protocols for monitoring and verification of the rate of SOC sequestration in a transparent, cost-effective, and credible manner for developing a user-friendly C trading system.
- Quantifying soil C sequestration potential for diverse land use and management scenarios at regional and national levels.
- Providing research information on soil C sequestration and the corresponding rates under "on-farm" conditions for recommended land use and management practices.
- Identifying processes of soil C sequestration (e.g., aggregation, humification, formation of secondary carbonates), and assessing the residence time of C thus sequestered.
- Developing the cost-effective, credible, transparent, and simple methods of measuring the rate of soil C sequestration that can be used for trading C credits.
- Identifying and implementing policy interventions for promoting sustainable land use/land use change and soil management practices that are a net sink for C.

- Evolving holistic land use and soil management package(s) for creating a positive ecosystem C budget and sustained and high rate of C sequestration.
- Including the component of CA practices in soil quality index card for proper monitoring of CR retention/burning and its impact on soil C sequestration and soil quality.
- Promoting C-positive technologies through extension organizations, state agricultural departments, and NGOs for farmer-driven programs.

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CHAPTER SIX

The Influence of Volcanic Tephra (Ash) on Ecosystems

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Contents

Abstract

Volcanic eruptions affect a large proportion of Earth's ecosystems, ranging from subtle dust inputs to thick deposits near the volcanoes. In this chapter, multiple influences of tephra deposition on land are investigated, using examples of recent volcanic eruptions. "Tephra" is the collective term for airborne volcanic materials, while ash is restricted to

Advances in Agronomy, Volume 121
ISSN 0065-2113
http://dx.doi.org/10.1016/B978-0-12-407685-3.00006-2

materials <2 mm in grain size. Impacts of tephra is depended on the nature of the tephra, including crystallinity, chemical composition, and grain size. The interaction between vegetation height and the deposition depth has a major influence on impacts, while surface roughness and other factors are also important. Low growing Arctic, alpine, and desert ecosystems are much more sensitive than higher vegetation and forests. Recovery time ranges from few to >1000 years. Alien species can severely interfere with ecosystem recovery. Erosion processes contribute to volcanic impacts by redistributing tephra, thus reducing tephra thicknesses in some places, but can also cause erosion rates exceeding 100,000 t km^{-2} $year^{-1}$. Wind erosion of tephra affects ecosystems, agriculture, and health but can provide beneficial dust inputs afar. Thick tephra deposits have pronounced impacts on agriculture, and F toxicity is common in volcanic areas. Soils that form in parent materials dominated by volcanic ash are mostly Andisols with the colloidal fraction dominated by short range order minerals and metal–humus complexes. Andisols are often fertile soils with a high capacity to accumulate carbon. There is a need for multidisciplinary long-term research on impacts and responses to volcanic eruptions.

1. VOLCANISM: THE FIRE THAT COOLS THE EARTH

1.1. Fire below

Volcanic activity has a pronounced influence on the world's ecosystems. Airborne volcanic materials are dispersed over large areas, with a vast range of consequences, spanning the creation of new surfaces to mild inputs of volcanic ash far from the erupting volcano. Volcanic eruptions have had a detrimental effect on the natural history of Earth through geologic time by affecting the composition of the atmosphere, climate, and geochemistry on the surface. Some of the single largest volcanic eruptions may have had significant effects on the biological evolution by causing volcanic (or "nuclear") winter conditions and mass extinctions (e.g., Rampino and Self, 2000; Robock, 2000), such as volcanic events at the Trias–Jura boundary (Ruhl et al., 2011), the eruption in Yellowstone about 640,000 years ago (e.g., Francis and Oppenheimer, 2004), and the more recent eruption in the Toba volcano (Indonesia) about 73,000 years ago (e.g., Mason et al., 2004; Williams et al., 2009). Volcanic eruptions are, fortunately, much more subtle on average with the main influences occurring in the vicinity of the volcanoes.

The current Smithsonian Institute Catalog of Active Volcanoes lists 1545 volcanoes that are known to have been active over the past 10,000 years but that it is "inescapably incomplete record" (Siebert et al., 2010). The

catalogue lists >9000 eruptions. There are about 70 volcanoes active each year on average but only 1–2 that produce >0.1 km^3 (Siebert et al., 2010). Ash clouds occur over the North Pacific every 1.25 months (Webley et al., 2012), which gives an idea of the frequency. Volcanic eruptions occur in Iceland on average every 4–6 years while the frequency at the Hawaiian hotspot is even greater (Thordarson and Höskuldsson, 2008). Some volcanic eruptions receive more attention than others, especially exceptionally, large eruptions and eruptions occurring in densely populated areas (Siebert et al., 2010). There is a wealth of literature on volcanic geology, which is, for the most part, too specific for this chapter. A number of textbooks on volcanic geology can aid the general reader, such as by Blong (1984), Francis and Oppenheimer (2004), Marti and Ernst (2005), Dale et al. (2005a), and the *Encyclopedia of Volcanoes* (Sigurdsson et al., 2000).

1.2. Distribution of volcanic activity

The volcanism on Earth is closely related to plate tectonics (see Perfit and Davidson, 2000); the gradual movement of the crustal plates, with the majority of the volcanism occurring close to the margins of the plates (Fig. 6.1). Notable examples are the Pacific "Ring of Fire" in both the Americas and in Asia, the African Rift-Valley, and the Mid-Atlantic Ridge. Plate movements can be thought of as cooling of Earth by conveying the inner heat to the surface or "plate recycling" (Francis and Oppenheimer, 2004).

There are important exceptions to the distribution of volcanoes along tectonic boundaries, such as cores of volcanic activity caused by so-called hot spots, which are driven by long-lived (millions of years) isolated plumes transferring heat from the mantle (e.g., Bjarnason, 2008). These plumes seem rooted in the mantle, while the tectonic plates gradually float over, creating island arcs and mountain ranges tracing the movement (e.g., Simkin and Siebert, 2000). Examples of hot spots are the islands of Hawaii, Galapagos, and Azores, but the Yellowstone volcanic system is an example of hot spots within continents or intracontinental volcanic activity. Iceland is an example where the occurrence of a hot spot coincides with a location under tectonic boundary of the rifting Mid-Atlantic Ridge (Einarsson, 2008).

1.3. Approach

Influences of volcanic eruptions on the ground are quite variable depending on the type of the eruption and the nature and volume of the deposited materials. In the most extreme cases, volcanic eruptions can obliterate the

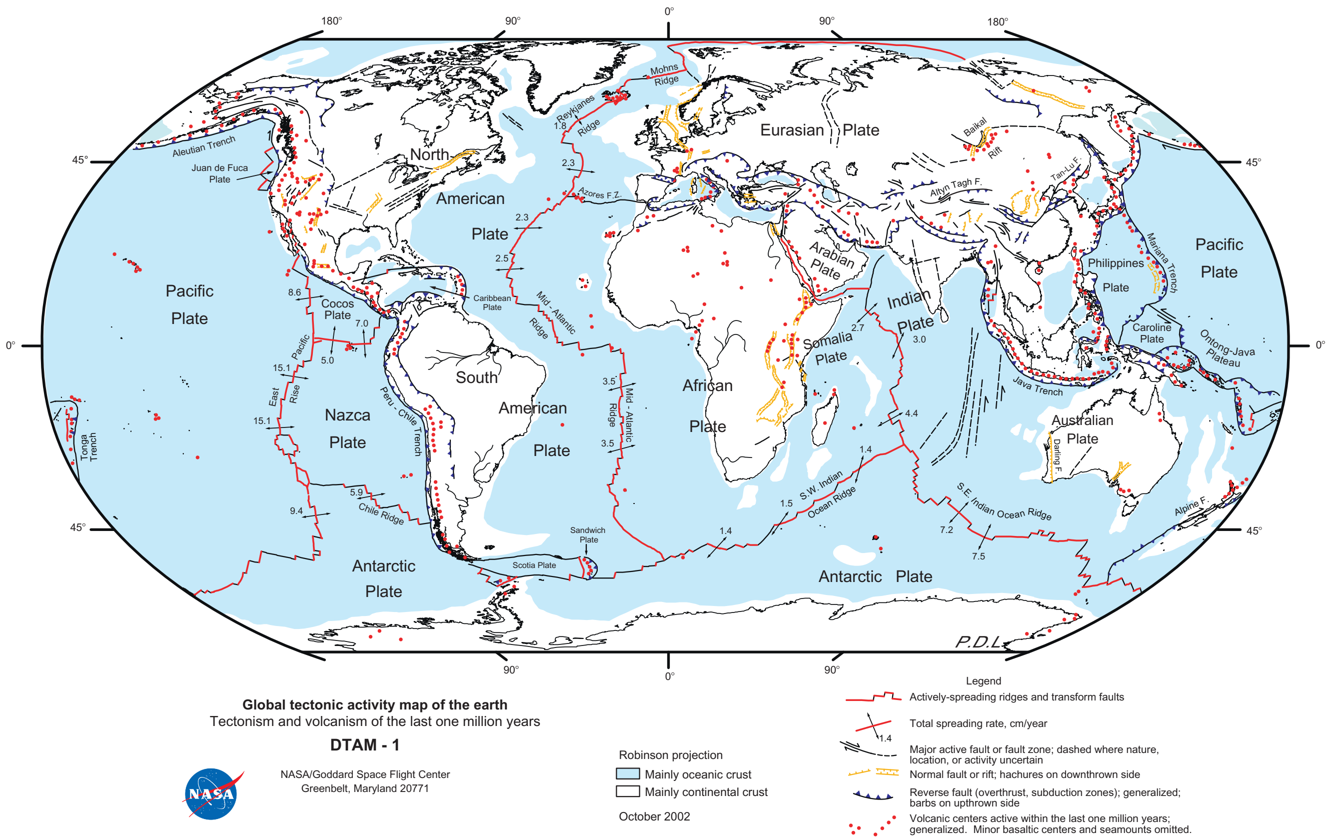

Figure 6.1 Plate tectonics and volcanic centers. NASA Goddard Space Flight Center Digital Tectonic Activity Map, NASA/Goddard Space Center. http://denali.gsfc.nasa.gov/dtam/

existing ecosystems to create new surfaces for primary succession. Thick volcanic deposits can have pronounced influences on the geomorphology of the affected areas, creating new topography and surfaces that are subjected to intense erosion processes by wind, water, and gravity. More subtle influences occur farther away from the volcano, as the deposits thin out to less than 1 mm, sometimes with positive effects on ecosystems. The diverse nature of volcanic impacts on ecosystems calls for multidisciplinary research approaches. The present chapter attempts to combine the subjects of soils, ecology, volcanology, geomorphology, and other disciplines into a single review paper on the effects of volcanic ash on ecosystems. In this chapter, multiple influences of volcanism on ecosystem are investigated, with emphasis on the ash deposits that result from explosive volcanic events. Other types, such as lavas and pyroclastic flows are mentioned for sake of completeness. A brief background on volcanic activity is also provided. The discussion is primarily concerned with "the present," meaning the past few thousand years during the Holocene, but one should bear in mind that much older magma and ash deposits still influence and even have overriding effects on soil systems and ecosystem functions in many volcanic regions. The chapter is not intended as a review of literature on volcanoes *per se* but to provide a background for those involved in scientific fields such as soils, agriculture, ecology, and related fields in areas affected by volcanic activity.

2. VOLCANIC ERUPTIONS, MATERIALS, AND DISPERSAL CHARACTERISTICS

2.1. Volcanic eruptions and tephra dispersal

The active tectonic belts account for >94% of all eruptions (Simkin and Siebert, 2000). Eruptions vary in energy and impact, and volcanologists have developed an index for the total volume of explosive products, the VEI (Voclanic Explosivity Index), with the VEI rising by a unit with 10-fold increase in explosive volume. As an example is the Mount St. Helens 1980 eruption rated as VEI 5 based on the explosive product volume (>1 km^3), Krakatau (1883) as 6 (>10 km^3), and Tambora (1815) as 7 (>100 km^3). The most common VEI of eruptions is 2 (about 50%), but small eruptions (VEI 0–2) account for about 80% of eruptions (Siebert et al., 2010).

The height of the plume determines in part the extent of the surface area impacted by a volcanic eruption, with plinian (VEI usually >3, column

height >3 km, >0.01 km^3 of products) and ultraplinian (VEI >5; column height >15 km, >1 km^3 of products) commonly affecting >1000 km^2 of land area (see Siebert et al., 2010). Wind characteristics during the eruption, such as speed and direction, influences where the tephra or ash is deposited (see Section 2.2.1 on terminology), creating thickness axes as shown in examples in Fig. 6.2A with the thickest deposits close to the volcano but thin deposits in extensive areas (Fig. 6.2B). Basaltic lavas have lower viscosities during eruptions but warmer eruption temperatures than the silicic (dacite, rhyolite). Average lava flow thicknesses range from 3 to 20 m for basaltic lava flows to >100 m for silica-rich lavas (Kilburn, 2000). Examples of volcanic eruptions, their size and impacts, are listed in Table 6.1.

There are several means of distribution of volcanic materials other than as lavas and direct tephra deposition, and the following terms are commonly used in this chapter.

Pyroclastic flows result from gravitational collapse of Plinian eruption columns or lateral explosions and from gravitational collapse of lava domes (Nakada, 2000). Often cited examples of such flows are the Vesuvius eruption (Italy), destroying Pompei 79 AD (Jashemski, 1979) and the Mount St. Helens explosion in 1980 (e.g., Dale et al., 2005b). Their extent from the volcano varies from few hundred meters to >100 km in the largest eruptions (Freundt et al., 2000). Deposits range from minor (<0.1 km^3) to the products of super-volcanoes exceeding 1000 km^3 of volcanic materials (Freundt et al., 2000).

Lahars are a mixture of solid volcanic materials and water brought down by gravity, and they are both a direct part of the volcanic events and post-eruptive phenomena (see Vallance, 2000). They are capable of traveling great distances of >100 km, often following existing waterways as was seen around Mount Pinatubo (Philippines) in 1991, which remobilized 3 km^3 of volcanic materials (Vallance, 2000). Millions of people live now in areas that have been affected by lahars during prehistoric times, including in the western USA (Rodolfo, 2000). Volcanic eruptions also produce "debris avalanches," as was observed during the eruption in Mount St. Helens, characteristically creating hummocky relief. Their deposits are often similar to lahar deposits (see Tadahide et al., 2000).

Jökulhlaups are lahar or flood events as a result of melting of ice during eruptions (Rodolfo, 2000), carrying high concentrations of volcanic materials. Such events can reach >100,000 m^3 s^{-1} discharge rates, and in Iceland, they have created vast sandy deserts exceeding 1000 km^2, often during repeated events (10s and 100s year intervals) (Björnsson, 2009; Björnsson and Palsson, 2008; Larsen and Eiriksson, 2008), with the sandy surfaces also maintained by aeolian

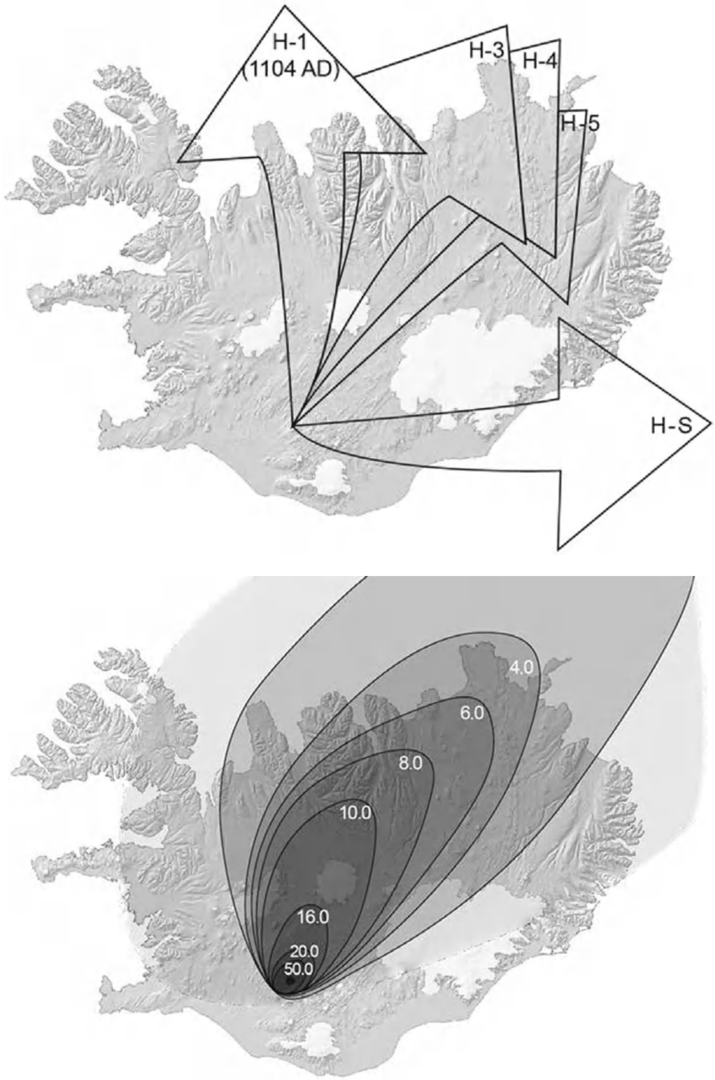

Figure 6.2 (A) Examples of multiple directions of tephra distribution from major silicic eruptions in Mount Hekla in Iceland during Holocene. (B) Example of a tephra distribution of the H3 Mount Hekla eruption (2800 BP); numbers indicate deposition thicknesses in centimeters. This was a major eruption with 11–12 $km^3$of tephra materials (Larsen and Thorarinsson, 1977). *(A) Adapted from Larsen and Eiriksson (2008) and (B) adapted from Einarsson (1991) and Thorarinsson (1961).*

Table 6.1 Examples of volcanic eruptions of different sizes and ages

Volcano	Year	VEI	Total (km^3)	Examples of impacts
Eyjafjallajökull (Iceland)	2010		0.2	Temporary air traffic shut down, vegetation burial, dust problems >2 years
Ruapehu (New Zealand)	1995–1996	3	<0.1	Severe fluoride toxicity problems, livestock killed
Pinatubo (Philippines)	1991	6	4–5	Temporary cooling, water erosion, and lahars
Hudson (Chile)	1991	5	4.3	Wide range of impacts on agriculture, dust problems
Mount St. Helens (USA)	1980	5	4.2	Pyroclastic flows, debris avalanches, lahars, and tephra
Hekla (Iceland)	1947	4	1	Tephra damage on rangelands, fluoride problems
Krakatau (Indonesia)	1883	6	10	Tsunami, tephra burial, and human casualties
Tambora (Indonesia)	1815	7	100	Catastrophic near volcano, >100,000 human casualties, global cooling with snow in England in June
Laki (Iceland)	1783	6	15–19	570 km^2 Lava buries farmland, toxic gas release and cooling, resulting in famine in Iceland and Europe
Santorini (Greece)	1610 BC	7	25	Destruction of Minoan culture, global draught, and famine
Toba (Indonesia)	73 k yrs	8	2700	"Volcanic winter" on Earth. Human genetic bottleneck?

VEI and year of eruption from Siebert et al. (2010). Volumes in km^3 dense rock equivalents. Impacts from Mason et al. (2004) (Toba), Thordarson and Höskuldsson (2008), Thorarinsson (1979) (Laki), Wilson et al. (2011a) (Hudson), Swanson and Major (2005) (Mount St. Helens), Cronin et al. (2003) (Ruapehu), Sigurdsson (2000) (Tambora), Lipman (2000) (Pinatubo and Santorini), Gudmundsson (2001) (Hekla), and Gudmundsson et al. (2012) (Eyjafjallajökull).

processes (Arnalds et al., 2001). The moderate (VEI 3) 1985 eruption in Nevado del Ruiz (Colombia), melted summit glacier that resulted in catastrophic jökulhlaups/lahars killing >20,000 people (Siebert et al., 2010).

2.2. Classification and terminology

2.2.1 Tephra and ash

The term "tephra" was introduced to the scientific literature by S. Thorarinsson in 1944, "to describe all pyroclasts that leave a volcanic vent by air, regardless of type, size, and shape" (see Larsen and Eiriksson, 2008). Tephra refers to materials that are primarily unconsolidated (Schmid, 1981). The term "volcanic ash" is often used quite loosely about all tephra materials but refers strictly speaking to tephra materials (or pyroclasts) that are less than 2 mm in diameter (Macdonald, 1972; see also De Paepe and Stoops, 2007). "Pyroclasts" and "pyroclastic rocks" are also common terms, pyroclasts being a broader term than tephra, including both consolidated and unconsolidated materials (Manville et al., 2009; Schmid, 1981), for "all material ejected from volcanoes as solid fragments" (Francis and Oppenheimer, 2004). A commonly used classification based on work by a scientific committee of the International Union for Geological Sciences (Schmid, 1981) is presented in Table 6.2, which also includes notions for various types of pyroclasts and tephra.

The term "tuff" is commonly used for consolidated pyroclasts, which has been recommended to be used for ash size particles only if used without other qualifiers, such as in "lapilli tuff" (Schmid, 1981). Pyroclastic flows and surges often form welded rocks or tuffs called "ignimbrites" (see Cas and Wright, 1987; Francis and Oppenheimer, 2004; Freundt et al., 2000). "Lapilli" is, according to this classification, coarse-grained (>2 mm) tephra. Common terms used for tephra deposits include "pumice," highly vesicular (porous) lapilli, which can be both silicic and basaltic in nature and will commonly float in water (Fisher and Schmincke, 1984). "Scoria" and "cinders" are also terms used for lapilli that will sink in water, usually basaltic in composition (Fisher and

Table 6.2 Grain size limits and terms for pyroclastic rocks

Size	Pyroclast	Mainly unconsolidated: Tephra	Mainly consolidated: Pyroclastic rock
>64 mm	Bombs, blocks	Agglomerate	Agglomerate, pyroclastic breccias
2–64 mm	Lapillus	Lapilli; lapilli tephra	Lapilli tuff
1/16–2 mm	Coarse ash	Coarse ash	Coarse ash tuff
<1/16 mm	Fine ash	Fine ash	Fine ash tuff

Simplified after Schmid (1981).

Schmincke, 1984). Is spite of efforts to harmonize the use of terminology, the terms and their meanings vary in the literature. Parameters such as the mean and median grain sizes, sorting, and skewness, are useful in differentiating between the tephra deposits, such as between pyroclastic flows and fall deposits, (Fisher and Schmincke, 1984; Heiken and Wohletz, 1985; Houghton et al., 2000; Manville et al., 2009; Walker, 1971; Wright et al., 1980). Manville et al. (2009) provided a review on developments in understanding volcaniclastics, showing a rapid increase in research papers on the topic and including a section on terminology and their different uses according to various schemes.

2.2.2 Crystallinity

The crystallinity of the material ejected from volcanic vents varies considerably, which again influences how the tephra impacts the surface and how the surface evolves after deposition. The crystallinity reflects the cooling history and the viscosity of the parent magma (e.g., De Paepe and Stoops, 2007). The term "vitric," which is drawn from Latin ("vitr" = glass), is used about non-weathered glassy tephra materials that are optically isotrophic (see De Paepe and Stoops, 2007). It is used as a diagnostic criterion for poorly developed Andosols/Andisols (IUSS Working Group WRB, 2006; Soil Survey Staff, 1999) and coins terms such as Vitrisols and Vitric Andisol. However, the degree of crystallinity (vitric vs. crystalline materials) varies considerably (Schmid, 1981). Pumice would most commonly belong to vitric materials, as do glass shards. Lithic materials contain larger rock fragments of various origins within the tephra deposits.

2.2.3 Chemical composition

The chemical composition of volcanic products depends on the nature of each volcanic system. Silica content is conventionally used as the classification criteria, but there are been many different ways of sorting igneous rocks further. A long-lasting effort by the Union of Geophysical Sciences (Le Bas et al., 1986; Siebert et al., 2010) resulted in the classification presented in Fig. 6.3, based on the silica and alkali content and is sometimes referred to as the "TAS (total alkali–silica) classification". All classification systems such as the TAS system presented in Fig. 6.3 have limitations, but the TAS system has proven quite suitable for igneous rocks, especially as mineralogical classifications, which are otherwise often preferred, cannot be applied for the noncrystalline tephra materials.

Basaltic eruptions (left in Fig. 6.3) are often nonexplosive (so-called effusive volcanism) or mixed, with more lava produced than volcanic ash. The

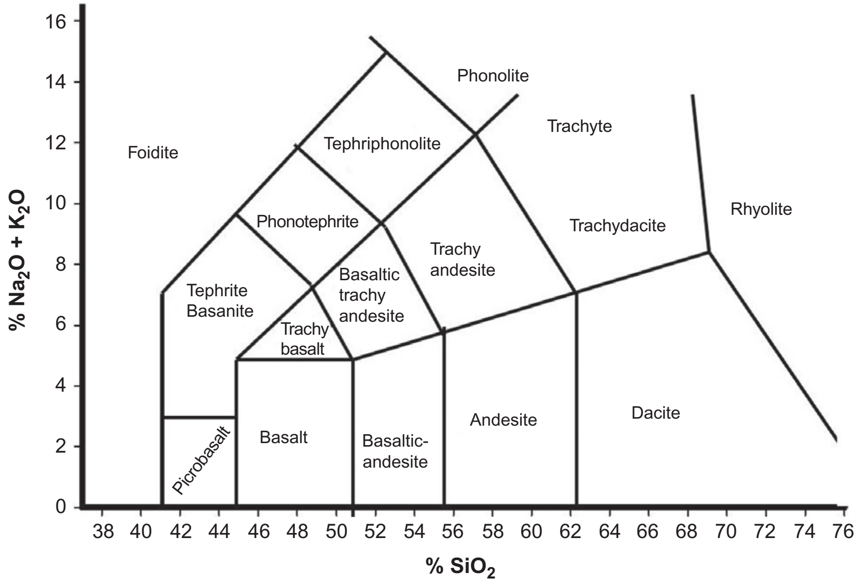

Figure 6.3 TAS (total alkali–silica) classification of rock types. Under each class various rock types occur (see Siebert et al., 2010), which can be divided further based on mineralogy, composition, texture, structure, and other factors.

large basalt shields are exemplary of such formations, as is the volcanism in Hawaii, and the large Laki eruption in Iceland in 1783, covering about 570 km^2 (Thordarson and Höskuldsson, 2008; Walker, 2000). Eruptions tend to get more explosive toward the silicic end of the composition, especially rhyolitic with $>70\%$ SiO_2 content (right in Fig. 6.3).

Explosive eruptions with production of tephra require fragmentation of the magma. There are several means for such fragmentation as reviewed by Cashman et al. (2000) and Morrisey et al. (2000) but most require that gas is released from the magma (dry explosive eruptions): "Magma is transformed from a foam of gas bubbles in silicate liquid into a rapidly accelerating stream of gas carrying pyroclasts" (Houghton, 2000). In some cases, water mixes with the lava, producing explosive eruptions that lead to tephra fallout (hence the term: wet explosive eruptions). Examples of this are volcanoes under glacier as in Iceland and islands rising up from the ocean (Morrisey et al., 2000; Thordarson and Höskuldsson, 2008).

2.2.4 Tephrochronology

Thorarinsson (1944) introduced the term "tephrochronology," for using tephra layers of known age for dating. Tephrochronology has proved to

be an extremely useful tool for a variety of research topics, as was recently reviewed by Lowe (2011). Tephrochronology has been applied in studies of pedogenesis, archeology, paleontology, geomorphology, dating and correlating volcanic events, and many more (e.g., Lowe, 2011). Good examples of how layers of tephra in soils are used to construct natural and human history are found in Iceland (Larsen and Eiriksson, 2008; Oladottir et al., 2011; Thorarinsson, 1981), where >150 eruptions have left markers in the Andisols over the past 1140 years since settlement. Sediments and soils at archeological sites can, therefore, be dated with some accuracy, including the Norse settlement, and the soils and pollen provide evidence for the climatological, ecological, and pedological history during the Holocene (Gisladottir et al., 2011; Hallsdottir and Caseldine, 2005; Streeter et al., 2012). Payne and Blackford (2008) suggested, on the other hand, that the effects of distal tephra layers in peatlands could be misinterpreted as changes caused by climate change and palaeoecological studies should include search for tephra layers.

3. IMPACT OF VOLCANIC ERUPTIONS

The nature of impacts caused by volcanic eruptions is quite variable as can be expected from the diversity in the amount and characteristics of the ejected materials and the nature of the impacted systems. The distance from the erupting volcano and the ability of the affected ecosystems to respond to the disturbance differ between volcanic events and ecosystems. The fate of the tephra after deposition is also important to consider, as it is subjected to compaction and redistribution by erosion processes. In this discussion, ecosystem recovery is taken as establishment of a functional ecosystem of comparable productivity as existed before (but not necessarily same or similar composition), covered with vascular plants and with soils capable of cycling nutrients and water.

The different types of impacts on the surface are listed in Table 6.3. It should be noted, however, that impacts from each eruption can be of numerous types which can be difficult to separate in the field, especially long after the events (see e.g., Dirksen and Dirksen, 2007).

3.1. Lava flows, thick pyroclastic flows, and other major impacts

3.1.1 Lavas and pyroclastic flows

The impact of an eruption can be expected to be the greatest next to the volcano, such as by lava flows, pyroclastic flows, lahars, and thick tephra

Table 6.3 Overview of impact types, disturbance, and aftermath of events

	Impact type	Ground disturbance	Aftermath, common year ranges	Examples
A	Lava flow	Destruction: new surface	New soil development, climate dependent, 100s to >1000 years	Hawaii; Mt. Etna; Laki, Iceland; Paricutin 1943–1990 (Mexico)
B	Pyroclastic flow, lahar, jökulhlaup	Total destruction: new surface	New soil development, climate dependent, 100s to >1000 years	Mount St. Helens Pinatubo, Philippines
C	Excessively thick tephra >70 (100) cm	Near total destruction: new surface, massive erosion	New soil development, climate dependent, 100s to >1000 years	Krakatau 1883 Ksudach, Kamchatka
D	Very thick tephra 20–70 (100) cm	Agriculture and rangeland destruction; massive erosion	20 to >100 years for recovery, shorter for forests	Katmai 1912, Alaska
E	Thick tephra 10–20 cm	Temporary disturbance; erosion and dust emission	Recovery 30–150 years on rangelands, shorter in forest, "permanent" in Arctic and desert areas, temporary disruption of cultivation (1–10 years)	Mount St. Helens 1980, Hudson 1991, Chile Paricutin 1943–1990 (Mexico)
F	Moderately thick tephra: 1–10 cm	Little and temporary disturbance, some erosion and dust emission	Temporary impact, species changes, 10–50 years for recovery of natural systems, positive nutrient responses[a]	Mount St. Helens 1980. Common in Iceland
G	Thin tephra: 0.1–1 cm	Little and temporary disturbance, erosion and dust emission	Sometimes positive nutrient responses, negative impact on crusts	Common in Iceland, Mts. Hekla and Katla

Continued

Table 6.3 Overview of impact types, disturbance, and aftermath of events—cont'd

	Impact type	Ground disturbance	Aftermath, common year ranges	Examples
H	Traces (<1 mm)	Negligible ground disturbance	Positive nutrient responses, temporary fluoride hazards	Widespread in volcanic areas
I	Gas/ash into tropo- and stratosphere	Regional—global cooling; eruption size dependent	Cool periods, crop failures, years	Laki, Iceland; Pinatubo, Philippines
Secondary impacts				
J	Aeolian redistribution, dust production	Abrasion and burial of plants, dust pollution	Continuous wind erosion dependent on thickness, 1–20 years	Eyjafjallajökull; Iceland in general
K	Fluvial redistribution[b]	Plugs up river channels, new areas for aeolian processes	Flooding, dust production, 1–10 years	Eyjafjallajökull, Pinotubo, Mount St. Helens
L	Landslides[b]	Dangerous in urban areas	Temporary disruption of natural systems, 1–20 years	Vesuvius

The depth intervals used for tephra thicknesses are examples but influences inevitably vary from site to site. Year intervals for recovery are indicative for temperate to subtropical conditions. Arctic and desert areas need longer time. The table is based on the reviewed literature but also draws from a table on the USGS Volcanic Ash Website showing the impact of volcanic ash on vegetation and soils (USGS Ash Web Team, 2012).

[a]Dependent on chemistry of the tephra.

[b]Other than those defined as lahar.

(A, B, and C in Table 6.3). These disturbances cause destruction of the existing ecosystems. Impacts from lava flows are common in areas such as Hawaii, around Etna (Italy), Paricutin (Mexico), and Iceland. The aerial extent of the lavas are controlled by the chemical composition and viscosity of the lava, total amount and discharge rate, together with landscape factors, such as the slope angle (e.g., Peterson and Tilling, 2000). The more silicic and thicker lava flows usually have more limited extent compared to the viscous basaltic lavas. A good example of large scale impact from basaltic lava flow is the Laki eruption in Iceland in 1783, where the fissure released 12–16 km^3 of basaltic lava that covered >500 km^2 of land, including prime

farmland (Thorarinsson, 1979). Similarly, pyroclastic flows destroy the ecosystems in their path, and they include some of the most detrimental volcanic disasters in history (Nakada, 2000). The resulting deposits vary in depth and other characteristics that affect new development of soils and vegetation. The temperature of the freshly deposited materials determines if the rock becomes welded as tuff or ignimbrite rock (see Freundt et al., 2000), which makes ecosystem recovery more difficult.

Ecosystem recovery of new surfaces created by lavas and pyroclastic flows involves primary succession with the development of new soils, while more subtle effects by tephra deposition result in secondary succession responses (e.g., Zobel and Antos, 1997). Recovery time is given in 100s and 1000s of years in Table 6.3. Weathering rates are partly controlled by climatic factors with more rapid weathering taking place in warm and humid areas compared to dry or cold regions. The recovery of lavas is dependent on the chemical composition and hardness of the lava, with basaltic lavas generally more easily weathered. Cutler et al. (2008) mention decades for "pioneer colonization stage" of moss growth in Mount Hekla lavas (Iceland, andesite, cold–humid climate), with "higher plant colonization stage" of 100–600 years and a "differentiation stage" after 600 years. Recovery is also dependent on the availability of seeds and safe sites for germination. Additions of loose sediments by fluvial or aeolian processes can enhance recovery by providing more suitable growth media on the more solid surfaces, including ash (del Moral and Grishin, 1999; Kiilsgaard et al., 1986), which is a major factor in ecosystem development in Iceland (Arnalds, 2010).

3.1.2 Lahars and jökulhlaups

Lahars, a mixture of solid materials and water, can be equally hazardous as lavas and pyroclastic flows. Debris avalanches create similar effects on the surface. These processes reshape topographic features by filling up waterways and even valleys. The sediments are, however, usually not as solid as those produced by pyroclastic flows. The impacted areas also tend to be narrow, resulting in short distance of transport of plant seeds and animals into the area, which facilitates shorter recovery time after the event. Recovery on Mount St. Helens lahars was strongly dependent on landscape factors such as elevation and isolation from other vegetation (e.g., del Moral et al., 2009). Blocks of soils and root wads also provide materials that enhance regeneration (del Moral and Grishin, 1999). After 28 growing seasons, colonization of conifers was well underway in lahar channels on Mount St. Helens, especially at lower elevations (del Moral et al., 2009). Marler

and del Moral (2011) reported fast recovery rate after the Mount Pinatubo eruption, under tropical lowland climate conditions, with dense vegetation cover in river valleys on 15-year-old lahars. The recovery was, however, compounded by the spread of exotic species.

Recovery in areas affected by jökulhlaups can been slowed by several factors, as exemplified by Icelandic conditions (100s–1000s of years) owing to the instability of the resulting surface, reoccurring flood events, lack of seeds and safe sites for seedling establishment, domestic animal grazing, and the cold climate of the impacted areas (Arnalds et al., 2001; Marteinsdottir et al., 2010).

3.2. Impact of tephra deposition

3.2.1 Responses of plants to burial: General considerations

Studies on sediment burial of vegetation have primarily dealt with redistribution of sediments caused by wind erosion resulting in aeolian deposition in coastal areas and desert environments (e.g., Jia et al., 2008; Maun, 1998; Maun and Perumal, 1999; Okin et al., 2006). Survival of vegetation subjected to aeolian and volcanic deposition depends on factors such as burial depth, the height of the vegetation, frequency of deposition events, time of year, vegetation composition and the ability of the plants to respond in various ways, influence of burial on vegetation competition, and nutrient transfer from damaged to surviving plants (Aradóttir et al., 2010; Hotes et al., 2010; Kent et al., 2001; Maun, 1998; Owen et al., 2004; Zobel and Antos, 1992, 1997). Burial affects oxygen flow to the underlying zone (Maun, 1998), but tephra characteristics are important in this context with fine materials and compaction more likely to reduce oxygen flow. Buried plants are deprived of sunlight for photosynthesis and growth and must, therefore, rely on their reserves if possible for growing up through the tephra deposits, with increased elongation of apical meristem, upward growth of apices, rhizomes, and shoots (Maun, 1998). Response capability is in part related to the amount of energy stored in buried underground parts (Perumal and Maun, 2006). Annual plants without reserves are temporarily wiped out, with regeneration depending on seed rain and safe sites for seed germination and emergence (e.g., Swedberg, 1986). Restrained oxygen flow affects microbial activity, nutrient cycling, and regrowth of surviving plants. Those plants that succeed in survival have a chance to utilize some of the nutrient base that would otherwise be used by others or becomes available with decomposition of dying plants, especially nitrogen (e.g., Gilbert and Ripley, 2008). The aboveground parts of the plants can also be damaged by the tephra, although they are not buried. As an example

reported by Antos and Zobel (2005) and Seymour et al. (1983), initial damage of tree–leaves when they were embedded in tephra and died from solar heating.

Maun (1998) presented a model for plant response to burial: in class I, species show negative response and die after burial; species in class II show no response initially with continued growth until deposition reaches above a certain level, where the response becomes negative; species in class III show positive response, which is common for plants adapted sand dunes. Such plants are often stimulated in several ways by the burial, such as by remobilization of buried leaf resources and shift in biomass allocation to stem production (see also Gilbert and Ripley, 2008). However, every plant species has a tolerance limit (Maun, 1998). Owen et al. (2004) provided a similar model with plants having five types of responses after 5 cm burial by sand, from relatively unaffected species and species that benefit from the deposition, species showing post burial recovery or eventual decline, to species that do not survive (type 5). Volcanic areas differ from sand accumulation areas in that burial events are likely to be rare compared to burial events in the dune environment, thus species tolerant to burial (class III in Maun's model) are less likely to occur.

3.2.2 Vegetation height

While the ability of the ecosystem to recover following tephra deposition is dependent on a complex interaction between abiotic and biotic parameters, vegetation height is often the most important single factor in volcanic areas, with vegetation types ranging from soil crusts, lichens, and mosses to tall-growing forests. A conceptual model for the interaction between vegetation height and the severity of impact is presented in Fig. 6.4. The model only considers systems that are not adapted to frequent burial events. It is important to bear in mind that there is a difference between species in response and survival and between communities, but this model considers response of communities or part of communites and their ability to recover. However, this relationship may not hold in forests where relatively thick deposition (e.g., >70 cm), but still only a fraction of the height of the forest, can have very detrimental effects to understory vegetation (e.g., Zobel and Antos, 2009) and the trees (e.g., Tsuyuzaki and Haruki, 1996).

Many studies of ecosystem response to burial involve field plot studies where sand or tephra materials are applied to the surface in different thicknesses. Martinez and Maun (1999) studied burial of dune mosses and developed a tolerance index to compare burial responses. They showed that some

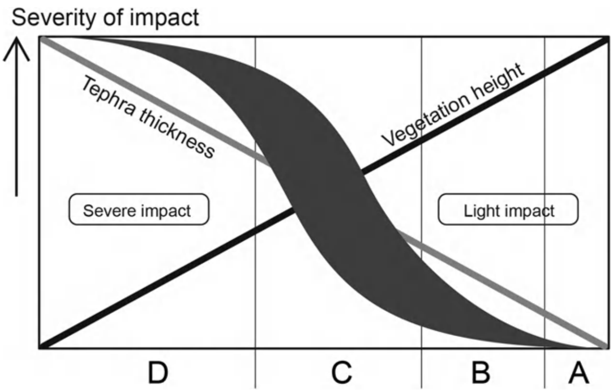

Figure 6.4 Conceptual drawing showing the interaction between vegetation height and tephra thickness on the severity of the impact (broad shaded line). The severity of the impact rises steeply as the tephra depth becomes about ¼–½ of the vegetation height. The exact location of the line for impact severity varies between systems with vegetation tolerant or adapted to burial placing the line more to the left. (A) Little or positive impact, limited vegetation changes. (B) Composition changes with species tolerant to burial increasing in abundance but temporarily reduced vegetation cover. Mainly secondary succession following the disturbance. (C) All species affected and many lost, long-term composition changes, both primary and secondary succession. (D) Long-term damage, primary ecosystem succession.

of the coastal mosses can tolerate up to 35 × burial compared to their height, while inland mosses showed limited tolerance. Aradóttir et al. (2010) studied vegetation of Arctic systems in Iceland under field conditions with 1–8 cm burial and showed that the low growing vegetation (1.7–3.1 cm mean height) was vulnerable to small amounts of deposition but with plants responding according to all classes (I–III) of Maun's (1998) model. Mosses and lichens are extremely vulnerable to even smallest tephra additions under the Icelandic conditions (Aradóttir et al., 2010; Magnusson, 1994; Vilmundardottir et al., 2009). A study by Vilmundardottir et al. (2009) of a natural burial event in the Icelandic highlands showed that the critical depth of burial for heathland vegetation was about 10 cm.

The thickness values in Table 6.3 refer to deposition thicknesses. While average deposition thicknesses are important, the redistribution in the aftermath of eruptions can make such numbers less meaningful, especially where the tephra deposition is thicker than the impacted vegetation (e.g., Major et al., 2000; Wilson et al., 2011b). This also applies where volcanic ash is deposited on surfaces with limited vegetation growth (e.g., Arctic, alpine, deserts), where the fresh volcanic materials are subjected to both aeolian and fluvial processes (Arnalds et al., 2012; Thorarinsdottir and Arnalds,

2012). Furthermore, many ash deposits consolidate soon after deposition with rainfall, even to 1/3 of original thickness, making the deposits more compact and forming a crust that restricts plant growth (Antos and Zobel, 2005), which may also affects oxygen flow to the old surface. This effect is very dependent on the nature of the ash, with compaction more likely for relatively fine ash compared to coarse pumice as an example. Consolidation of tephra and subsequent redistribution also makes volume and mass estimates of deposited tephra difficult (see Houghton et al., 2000).

3.3. Ecosystem recovery after tephra deposition

The timeframe for ecosystem recovery can range from a few weeks to 1000s of years (Table 6.3). The factors that influence recovery rate after deposition of tephra are divided in Table 6.4 into volcanic, biotic, climatic and seasonal, and surface factors.

Under the most unfavorable environmental conditions, a full recovery is not achieved, even after 1000 years (e.g., thick tephra deposits, dry or cold climate) while full recovery is near after 10 years where conditions are favorable, such as when thin tephra falls on lush vegetation. It is, however, difficult

Table 6.4 Overview of factors affecting ecosystem recovery after tephra deposition

Volcanic	Biotic	Climatic and seasonal	Landscape/ surface
Thickness of tephra	*Ecosystem* Pasture/rangeland, forest, Arctic, alpine, desert, wetlands	*Rainfall* (amount and intensity), *wind speeds* (intensity of dry storms)	*Landscape* characteristics and *mosaic*, seed sources, etc.
Nature of deposits Chemistry, texture, hardness, compaction, toxicity	*Local vegetation* Height and composition, biological legacy	*Temperature* annual, growing season, etc. Includes also temperature gradients with height	Surface *steepness*, surface *roughness*, surviving *vegetation*, etc.
Distance from volcano Influencing grain size and thickness	*Adaption to burial*, that is, some plants adapted to burial, some vulnerable	*Time of year* with largest impacts at the beginning of growing season, least in the fall and on snow	*Isolation* distance from propagule sources
	Animals carrying seeds	*Snow cover* and intensity of snow melt events	

to define what is a full recovery. Many soil parameters, such as clay content, are still developing even under favorable conditions after 1000 years. Yet, productivity and ecosystem functions may be achieved much earlier, including water holding capacity and cycling, nutrient cycling, primary production, grazing tolerance, and even biodiversity can reach predisturbance levels in much shorter time. It is also worth noting that many systems in volcanic areas are subjected to repeated disturbances, and therefore, full development for thousands of years is never reached.

3.3.1 Thick tephra deposits, >10 cm

Thick tephra deposits have adverse effects on the ecosystem on the surface, but the impact and recovery is dependent on the relationship between factors such as climate, tephra characteristics, physical processes after deposition, and surviving components of the previous ecosystem (Table 6.4).

Grishin's et al. (1996) study of the impact of the 1907 Ksudach eruption (Kamchatka) and the different successional pathways found between different levels of impacts highlights the importance of vegetation height and type for survival. They found that 100 cm of pumice destroyed all vegetation, nearly all was killed within the 70–100 cm depth range while isolated patches of vegetation and isolated trees (birch) survived in 30–70 cm thick deposits. In deposits 20–30 cm, trees were damaged, but other vegetation was killed. In areas with 10–20 cm deposits, some dwarf shrubs and herbs survived also while the moss was killed. Deposition under 10 cm caused damage without eliminating species. Detailed studies of the vegetation development in areas buried by the immense Krakatau eruption in 1883 (Whittaker et al., 1989) show after a series of field campaigns that sites that where forested prior to explosion remain species-poor and composed of early seral species. But the area continues to be affected by persistent volcanic activity. Whittaker et al. (1989) further noted that species transported by animals account for the majority of increased vegetation.

On Mount St. Helens, 12–15 cm thick tephra from 1980 almost obliterated the herbaceous understory but 20 years later the sites differed in plant composition and had <60% of preeruption vegetation (Antos and Zobel, 2005; Zobel and Antos, 2007). Trees (>20 m height) receiving >1 m thick tephra at the caldera rim of Mount Usu (Japan) in 1977–1978 eruptions were severely affected (Tsuyuzaki and Haruki, 1996). However, erosion soon removed a large part of the tephra, which has allowed for relatively rapid tree recovery (years), with the surviving trees feeding on nutrient reserves in the buried topsoils and branches. Responses vary between tree species just

as for the lower vegetation. As an example had deciduous trees higher growth rates than conifers shortly after the deposition of Mount St. Helens tephra (Adams et al., 1986b).

Rees (1979) reported a total and nearly total kill zones with tephra >1.5 m for early phases of the 1943–1990 Paracutin eruption (Mexico), but tree damage and heavy kill of shrubs and herbs with 50–150 cm remaining tephra depth. At 15–50 cm tephra deposition, there was partial survival of vegetation. Inbar et al. (1994) noted that where there were more than 1 m deep tephra deposits after this eruption, sand dunes were formed with limited vegetation growth. Where water erosion was active, forests reappeared within decades, demonstrating the importance of redistribution processes following eruptions. Forests exposed to 25–50 cm ash during this eruption survived (Inbar et al., 1994). Wilson et al. (2011b) reported that more than 10 cm of tephra from the 1991 Hudson eruption (Chile) destroyed vegetation and suppressed regrowth, with subsequent severe erosion processes. Recovery of thick deposits in Iceland is slow in relatively cold climate, especially in the highlands (see Section 3.3.4). Another example of such slow recovery of thick tephra deposits was reported by Day and Wright (1989) showing limited plant cover on >2000 old coarse scoria deposits in Idaho, with slow recovery attributed to cold dry climate and the coarse unstable substrate. Both these examples show the importance of climatic effects on recovery (cold in Iceland, dry in Idaho).

The presence of forests has a major implication for stabilization of thick tephra and enhancing regrowth. With thick tephra deposits, there is initial nutrient deficiency for plant growth, especially nitrogen, but also P and other nutrients that undergo organic cycling (Shoji and Takahashi, 2002). Vitousek (1999) showed the benefit of P fertilizer applications for nitrogen fixation of young volcanic sites in Hawaii. The presence of nitrogen-fixing pioneer or colonist plants such as lupines can enhance recovery as reported by several authors, such as del Moral and Wood (1986) and Russell (1986) for Mount St. Helens recovery. Thornton (2000) noted in his review that "starter nitrogen" is needed, which can be of multiple origin, including early nitrogen fixers, cyaonbacteria, and organic airborne fallout (see also Fridriksson, 1975).

3.3.2 *Moderately thick tephra deposits, 1–10 cm*

The impact of 1–10 cm tephra deposition is strongly influenced by vegetation height. Hotes et al. (2006) investigated the impact of 0.5 to >25 cm thick tephra in soil strata on wetlands in Hokkaido (Japan) and found that

tephras <10 cm thick did not induce long-term shifts in peat forming plant communities. Antos and Zobel (2005), using 100 permanent plots affected by the 1980 eruption in Mount St. Helens, stated that even 2 cm of tephra buried small bryophytes, which regained their previous cover in 2–3 years. However, 4.5 cm burial (more initial thickness) required much longer time for new colonization of bryophytes by spores. Herbaceous species penetrated through the 4.5-cm tephra but 15-cm tephra nearly eliminated the herb layer (see also Zobel and Antos, 2007, 2009). However, 5–10 cm tephra at Mount St. Helens did not have more effect on primary production in subalpine meadows than weather fluctuations, although pronounced effects were found in composition and species diversity with community simplification (Pfitsch and Bliss, 1988).

Swedberg (1986) showed that 1.2–1.5 cm thick deposition of Mount St. Helens tephra (1980) on plant populations on shallow stony soils had some effect with winter annuals decreasing but perennial grass plants seemingly increasing. Mosses became more prevalent with lichens declining. Payne and Blackford (2008) also showed pronounced effects of thin tephra layers on peatlands from their study of palaeoecological evidence in Alaska. Hotes et al. (2010) made experimental burial of wetland vegetation in Hokkaido (Japan) with *Sphagnum* moss cover with tephra materials up to 6 cm thick. All plots recovered to a degree, but pathways of regeneration differed between functional groups depending on the thickness.

3.3.3 Thin tephra input, <1 cm

Vegetation of low stature is vulnerable to thin tephra deposition. Only 1–4 mm of sand burial of biological crusts in the Tengger Desert (China) had negative effects on the crusts, reducing respiration rates and moss shoot elongation (Jia et al., 2008). The negative effect was amplified by the lack of moisture, making the system more vulnerable to the disturbance. Similarly, in a cold environment, with low vegetation, 1 cm burial had negative effect in the Icelandic highlands (Aradóttir et al., 2010). Bilderback and Slone (1987) and Antos and Zobel (2005), in their investigation of Mount St. Helens impacts, noted that ash on tree foliage 113–480 km downwind caused only slight and temporary physiological changes, with increased surface fungal colonization.

Thin and distal volcanic deposits can possibly have a greater contents of volatiles absorbed on the surface (Oskarsson, 1980), which can produce both negative (e.g., toxic) and positive effects (nutrition) as suggested by Payne and Blackford (2008). Hall (2003) found no influence of thin Icelandic

mid-Holocene tephras on Irish wetlands and dryland taxa. Some of the beneficial effects of light tephra inputs are discussed in Section 5.4.

Thin volcanic deposits are often widespread and are important for tephrochrological studies. Thin layers are found well preserved in peatlands around the world (e.g., Hotes et al., 2001; Hotes et al., 2010; Payne and Blackford, 2008; Zoltai, 1988). Their origin can most often be traced to distinct volcanoes or volcanic systems based on chemical analysis (Lowe, 2011), for example, by Fe–Ti composition (Oladottir et al., 2008) and trace elemental composition (Oladottir et al., 2011).

3.3.4 Examples from Iceland

Iceland experiences frequent tephra deposition events, which is among the main reasons for about 40,000 km^2 of land with desert-like conditions in spite of a cold and humid climate. The deserts are partly maintained by grazing by sheep (Arnalds et al., 2001). Thorarinsson (1979) indicated that in the Icelandic lowlands, tephra >30 to 50 cm thick causes permanent land abandonment, while 15–30 cm causes 1–5 year abandonment. The Thjorsa valley area in Iceland was hit by 6 to over 30 cm thick tephra in eruption of Mount Hekla in 1104 AD, which caused major farm abandonment in parts of the valley, burying important archeological sites from the Viking period (Dugmore et al., 2007). Tall vegetation (trees) did, however, manage to grow through >30 cm tephra, allowing for continued land use. Dugmore et al. (2007) concluded, however, that the resilience of the land had already been impacted by land use and an 874 AD eruption and that land use was finally discontinued after another eruption in 1300 AD. This sequence provides an example of increased impact of repeated events, each reducing the ability of the systems to meet further impacts, often amplified by land use pressure. It is interesting to note that this valley still remains relatively barren >900 years later, owing to repeated tephra deposition events and continued grazing by sheep until recently.

Thorarinsson (1979) concluded that 0.5–1 cm tephra deposition in Iceland caused insignificant effects on vegetation (lowlands), but his statement was not supported by ecological research *per se*. A few centimeter-thick tephra from the Eyjafjallajökull eruption in Iceland (2010) had little and even seemingly beneficial effect on birch forest vegetation, both trees and understory (Oskarsson, 2011). However, few centimeter deposits on low growing vegetation had a detrimental effect, especially on mosses and biological crusts on flat surfaces, both because of the deposition and redistribution by wind (Arnalds and Aradottir, 2011). Redistribution of relatively thin deposits is

damaging, making the surface roughness an important factor in addition to vegetation height. Vegetation cover also affects infiltration rates after tephra deposition, influencing potential redistribution by water as discussed in Section 4. The Icelandic experience clearly shows the importance of maintaining strong vegetation cover close to volcanoes such as the native birch forests. However, land use has now reduced the vegetation cover and height in the vicinity of many of the active volcanoes, resulting in lower resilience and greater impacts even under low–moderate tephra additions.

3.3.5 Interaction between tephra deposition and exotic/alien species

Land use and the introduction of new species and species assemblies may influence the recovery of ecosystems after tephra deposition. del Moral and Grishin (1999) discussed how the presence of alien/exotic species changes the pathways of regeneration of ecosystems impacted by volcanic eruptions. Exotics dominate recovery after volcanic disturbance in New Zealand (Clarkson and Clarkson, 1983) and at tephra sites in Hawaii (Vitousek et al., 1987; Walker and Vitousek, 1991). Marler and del Moral (2011) showed how rapid recovery after the Mount Pinatubo eruption, under tropical lowland climate conditions, was compounded by the spread of exotic species. In Iceland, introduced Alaskan lupine (*Lupinus nootkatensis*) has been used for restoration purposes on sites disturbed by volcanic eruptions. Its use has become increasingly controversial (Petursdottir et al., 2013), but its spread may become facilitated by further volcanic disturbances. It is clear that the use of exotic invasive species should be avoided in volcanic areas unless their benefit and their effect on recovery and ecosystem development after eruptions are fully understood.

4. SECONDARY IMPACTS: EROSION

Erosion processes that occur after tephra fall events are critical for determining the overall impact on ecosystems and recovery trajectories. Manville et al. (2009) concluded that "sedimentary repercussions of volcanic eruptions can have more severe, far-reaching, and prolonged impacts than the initial volcanism." The intensity of these processes are subjected to many variables, including the depth and nature of the deposits, vegetation characteristics, surface roughness and steepness, and climatic parameters (see Table 6.4). The secondary impacts not only affect the tephra fallout areas, as redistribution can reach far with both water and wind, with dust being carried 100s and even 1000s of kilometer away from the sources.

4.1. Hydrology and water erosion

4.1.1 Infiltration

With noncohesive tephra in a mountainous terrain, often accompanied by destruction of protective vegetation cover, sediment loads become extremely high initially after eruptions. Tephra deposits can reduce infiltration rates within the affected areas, but the nature of the tephra, especially grain size and compaction, become quite important parameters. Slower infiltration rates are associated with fine-grained ash. Major and Yamakoshi (2005) reported reduced infiltration rates on 600 km^2 area near Mount St. Helens after the 1980 eruption, up to 50-fold on hillslopes, from >75 mm h^{-1} to few mm h^{-1}. The volcanic impact dramatically altered the landscape hydrology with increased peak flows, but infiltration rates remained 3–5 times slower 20 years after the eruption (Major and Mark, 2006; see also review by Swanson and Major, 2005). Leavesley et al. (1989) reported 2–5 mm h^{-1} infiltration rates on 20–35 cm tephra soon after the Mount St. Helens eruption with increasing rates the following year. The slowed infiltration causes surface runoff of the noncohesive tephra during high intensity storms and snow melt events in the area (Major and Yamakoshi, 2005). Adding tephra on top of vegetated system in Iceland can be expected to temporarily halt infiltration dramatically in winter, judging from measured rates (Orradottir et al., 2008); thus amplifying runoff during snowmelt events.

An example of rapid infiltration after an eruption comes from New Zealand, but the 1886 eruption in Tarawera, which deposited >50 cm of highly permeable basaltic scoria and ash on relatively flat area (White et al., 1997). Erosion was low and rill formation not substantial in these deposits (White et al., 1997). Volcanic eruptions can also impact groundwater as experienced by the 1943 Paricutin (Mexico) eruption (Rees, 1979).

4.1.2 Water erosion

Sediment yield can reach staggering proportions soon after eruptions with $>100{,}000$ t km^{-2} $year^{-1}$ after the 1990s eruption in Merapi and Semeru, Java (Lavigne, 2004), and up to $>1{,}000{,}000$ t km^{-2} $year^{-1}$ after the 1991 Pinatubo eruption (see Gran and Montgomery, 2005; Hayes et al., 2002). Kadomura et al. (1983) reported sediment yield up to 170,000 m^3 km^{-2} $year^{-1}$ after the Usu eruption in Japan 1977–1978, in part caused by mudflows. They stress the role of rapid snow thaw events. Similarly, Waythomas et al. (2010) found sediment yield of 17,000–120,000 m^3 km^{-2} $year^{-1}$ the first year after the 2008 eruption of Kasatochi Island, Alaska. Major et al.

(2000) reported as much as 500 times greater annual suspended sediment yields after the Mount St. Helens eruption. Suspended sediment yield from the debris avalanche deposits remained 100 times greater after 20 years from the impact (Major et al., 2000; see also Major, 2004).

Leavesley et al. (1989) showed that the development of rills exposes preeruption surfaces, which can be beneficial for recovery and that coarse tephra facilitates sheet erosion while surface crusting in finer materials gives rise to rill formation. Hayes et al. (2002), investigating fluvial sediment transport after the 1991 Mount Pinatubo eruption, suggested that massive disturbances "induce morphologic and hydrologic changes that temporarily enhance transport efficiency until the watershed recovers and sediment supply is reduced." Swanson and Major (2005) noted that discharge rates after the Mount St. Helens were reduced after about 5 years, with areas with channel disturbances recovering more slowly.

Deflation rates (the lowering of the surface) of >10 mm year^{-1} can be expected the first years after tephra deposition. Research on erosion in the vicinity of Mount St. Helens includes a variety of impact types, such as pyroclastic flows, lahars, and tephra deposition. Collins and Dunne (1986) measured 26 mm year^{-1} basin wide deflation rates the first year after the eruption in Mount St. Helens, which was reduced to 1.8 mm year^{-1} after 3 years, with the development of stable rill network and more permeable and less erodible surfaces. Interpretation of data presented by Helgason and Jensen (2011) indicates that deflation rates after the 2010 Eyjafjallajökull eruption in Iceland exceeded 50 mm in places during the first year. High rates of water erosion after volcanic eruptions have also been reported after the 1970s Usu eruptions on Hokkaido (Kadomura et al., 1983; Tsuyuzaki and Haruki, 2008). The high erosion rates from the slopes of volcanoes by water can result in devastating lahars, which can carry enormous amount of volcanic materials to lower grounds. Montgomery et al. (1999) emphasize that substantial sediment transport occurred after the Mount Pinatubo eruption even at low-flow conditions. The Icelandic jökulhlaups have similar sediment yields with peak flows in some cases of $>200{,}000$ m^3 s^{-1} (Eliasson et al., 2007). An example is the 1996 Skeidara river jökulhlaup after a Grimsvötn eruption, which peaked at about 50,000 m^3 s^{-1} with a total sediment transport of about 1.8×10^8 m^3 (Russell et al., 2006). Stabilizing the tephra to reduce water erosion has proven difficult in places, especially during the most active erosion stage, revegetation efforts after the Mount St. Helens eruption with grass cover were only successful after erosion had declined sharply (Collins and Dunne, 1988).

It should be noted here that many volcanic areas are prone to landslides long after the tephra has been deposited and after vegetation cover has formed, in part owing to the high water holding capacity and thixotropic nature of the soils, but tephra layers can also form slip planes on slopes (e.g., Basile et al., 2003).

4.2. Wind erosion and dust

Aeolian processes include deflation, sediment transport along the surface, airborne dust (suspension), and sedimentation caused by wind erosion (Bagnold, 1941). Aeolian processes damage ecosystems and often prevent natural regeneration of vegetation (Armbrust and Retta, 2000; Maun, 1998). Reports of wind erosion in the literature in relation to volcanic impacts seem less common compared to reports of water erosion. Edgett and Lancaster (1993) reviewed the occurrence of volcaniclastic sand-fields and dunes, which range from silicic to mafic in composition. They gave examples of silicic sandfields in Oregon, California and New Mexico, andesitic in coastal dunes of New Zealand, in Washington, Arizona, Hawaii and Iceland, and basaltic dunes in Peru. Iceland has the largest volcanic sandfields covering $>$21,000 km^2, with intense wind redistribution of volcanic materials (Arnalds et al., 2001).

Movement of sediments by wind occurs by three main modes (see e.g., Ravi et al., 2011). The collision of moving particles causes new ones to be lifted up briefly before they hit the ground, causing further collisions. This bouncing movement of materials is called saltation and usually involves silt to fine sand-sized particles. This is the most erosive form of wind erosion and moves the largest share of particles, but the ratio depends on grain size distribution and other surface characteristics. The smallest particles (fine silt–clay) become suspended as dust and can be carried away long distances from the source area (Lawrence and Neff, 2009). Some grains or clods of soils are too coarse to be moved by wind (often near 1 mm size limit with 0.84 mm used in equations; e.g., Ravi et al., 2011; Skidmore, 1994), and some of these are pushed along the surface (surface creep). However, the light density of some tephra materials, with grains even $<$1 g cm^{-3}, results in that much larger grains can be moved by saltation. Grains that are several millimeter in diameter move by saltation in Iceland (Thorarinsdottir and Arnalds, 2012). Furthermore, the saltation layer extends much higher under these conditions or $>$100 cm (Arnalds et al., 2012; Thorarinsdottir and Arnalds, 2012) compared to 20–30 cm height limits reported for more conventional conditions (Pye and Tsoar, 1990; Zhang et al., 2007). With wind reworking the tephra surface, smaller grains are gradually removed from the sediments.

Wilson et al. (2011b) measured greater grain size for the tephra 17 years after the 1991 Hudson (Chile) eruption. The volcanic glass tends to be hard and abrasive (e.g., Cas and Wright, 1987).

Units of measurements for aeolian processes vary. The widely used Wind Erosion Equation and similar equations (see e.g., Fryrear, 1990; Skidmore, 1994) use tons of soil lost from each hectare as the response value, while transport can be measured as amount over a meter line, often during a set time (e.g., $t\ m^{-1}\ h^{-1}$; Arnalds et al., 2012) or through an area (e.g., $kg\ m^{-2}$; van Donk and Skidmore, 2001). Atmospheric dust is commonly measured as concentrations ($\mu g\ m^{-3}$, e.g., Engelstaedter et al., 2006), and deposition as weight per unit area (e.g., $g\ m^{-2}\ year^{-1}$; Arnalds, 2010), or sedimentation rate ($mm\ year^{-1}$; Thorarinsson, 1961).

An example of wind erosion after a volcanic eruption is the aftermath of the 1991 Hudson eruption in Chile. The eruption affected about 100,000 km^2 of Patagonia, with strong winds causing "billowing clouds of remobilized ash" and impacts of staggering proportions (Wilson et al., 2011b). The continuing storms caused burial of farmland and vegetated areas and severe health problems for humans and animals. Wilson et al. (2011b) further noted that the tephra blanket reduces surface roughness, enhancing wind erosion processes and that the greatest erosion is expected in areas of maximum exposure, such as on ridges or where high winds can be expected. They report that wind-blown ash remained as a severe problem for 4–6 months.

Wind erosion was important in redistribution of materials following the 1943–1990 Paricutin (Mexico) eruption while fluvial process subsequently became dominant (Inbar et al., 1994). Tephra deposition during eruptions and jökulhlaups are a major cause for formation of deserts in Iceland (e.g., Arnalds et al., 2001, 2012). The magnitude of saltation of volcanic materials commonly reaches $>500\ kg\ m^{-1}$ in one storm and yearly saltation transport often exceeds $3000\ kg\ m^{-1}\ year^{-1}$. After the Eyjafjallajökull eruption in 2010, about $10{,}000\ kg\ m^{-1}$ transport was measured in one storm with gusts $>38\ m\ s^{-1}$ (Arnalds et al., 2013b). Deflation rates of 20–50 mm and sediment yields of the magnitude $10^5\ t\ km^{-2}$ can be inferred from the data published by Arnalds et al. (2013b). Under these conditions, wind erosion is of the same order as extreme sediment yields from water erosion after volcanic eruptions. The unstable volcaniclastic materials cause losses of fully vegetated systems and prevent ecosystem recovery within the impacted areas. The materials are the source of ash storms that impact humans and animals in Iceland (Arnalds, 2010; Arnalds et al., 2001, 2012; Thorarinsdottir and Arnalds, 2012). Thorarinsson (1979) noted that >18 farms, utilizing

subarctic highland vegetation in Iceland, were abandoned after receiving >15 cm of tephra fall from the Askja volcano in 1875. This abandonment "was caused chiefly by soil erosion by wind and water," damaging the surviving vegetation. Lava fields accumulate redistributed tephra, their capacity depending on the lava roughness (Gisladottir et al., 2005). The tephra sediment accumulations in depressions are often a bed for vegetation succession as seen after the 1943–1990 Paricutin eruptions (Inbar et al., 1994).

Dust blowing from volcanic areas has similar effects as trace depositions during eruptions far from the volcano. Dust can, in general, have far-reaching effects on soil formation, fertility, and human health (Buzea et al., 2007; Lawrence and Neff, 2009). The severe dust storms following the previously mentioned 1991 Hudson eruption in Chile (Wilson et al., 2011b) caused partial evacuation of small rural towns and had pronounced effects on agriculture and ecosystems. The glaciofluvial plains of Iceland, which are recharged during volcanic eruptions (jökulhlaups) and other flood events near the volcanoes, serve as a continuous source of aeolian materials deposited over the terrestrial Iceland and surrounding oceans at a rates of 10–500 g m^{-2} $year^{-1}$ (Arnalds, 2010). This leads to sedimentation rates from 0.01 to over 1 mm $year^{-1}$ and has a major impact on soil and ecosystem development in Iceland. These dust storms are of global scale, producing dust that reaches far over the North Atlantic (Arnalds, 2010; Prospero et al., 2012). Redistribution of volcanic dust caused high levels of air pollution in Iceland after the 2010 Eyjafjallajökull eruption, even >100 km away from the volcano, with suspended particulate concentrations (PM_{10}) repeatedly exceeding 1000 μg m^{-3} (e.g., Leadbetter et al., 2012). Horwell and Baxter (2006) reviewed respiratory health hazards after volcanic eruptions and concluded that a more multidisciplinary systematic efforts were needed.

The chemical composition of the dust can be harmful, especially if blown soon after the deposition, causing floride (Cronin et al., 2003; Oskarsson, 1980) and heavy metal problems (Buzea et al., 2007; Horwell and Baxter, 2006). However, wind erosion of volcanic materials also contributes to rejuvenation of nutrient supply (see Section 5.4) just as wind erosion in other areas (see e.g., Poortiga et al., 2011).

5. VOLCANIC ASH AND SOIL DEVELOPMENT

5.1. Andisols

Development of soils after deposition of tephra depends on factors such as vegetation survival and succession, nutrient accumulation and the

interaction between vegetation, soil nutrients and water, and other factors. One of the most distinct influences of volcanic ash on the environment is the development of unique soils, Andisols. Andisols have unique characteristics and properties with a host of environmental attributes that affect fertility and hydrology (Shoji and Takahashi, 2002). Most Andisols develop in relatively thick deposits, but ash deposition also influences other soils, depending on the deposition thicknesses and other factors. Many of the unique properties of volcanic soils have been investigated in detail, together with work that spans most volcanic regions of the world, reported in several books and review papers Dahlgren et al., 2004 in *Advances in Agronomy*; Fernandez Caldas and Yaalon, 1985; (Maeda et al., 1977; Shoji et al., 1993a; Wada, 1985; Arnalds et al., 2007; Arnalds and Stahr, 2004; Bartoli et al., 2003; McDaniel et al., 2011). However, this chapter is not intended as an exhaustive review of volcanic soils but to highlight some main issues in relation to recent volcanic ash deposits.

The U.S. Soil Taxonomy (Soil Survey Staff, 1999; see also Parfitt and Clayden, 1991; Shoji et al., 1996) and the WRB classification (IUSS Working Group WRB, 2006) of volcanic soils are based on the same principles and use many of the same diagnostic criteria (Shoji et al., 1996). It should, however, be noted that soils with similar properties as Andisols and even soils that classify as Andisols can develop outside volcanic regions (e.g., Baumler and Zech, 1994; Garcia-Rodeja et al., 1987; Hunter et al., 1987), but these are exceptions not being considered here.

5.2. Weathering of volcanic ash: Genesis

Most of the unique properties of Andisols are related to their colloidal fraction. Allophane, imogolite, and ferrihydrite clay constituents have a varying degree of crystallininty, hence non-consistent use of terms such as "non-crystalline," "poorly-crystalline," and "short-range order," "materials," "minerals" or "clays," which sometimes causes confusion for those more familiar with the conventional layer silicates (see Dahlgren et al., 1993, 2004; McDaniel et al., 2011; Parfitt, 1990; Parfitt and Kimble, 1989; Ugolini and Dahlgren, 2002). Parfitt (1990) gave the following definition of allophane: "Allophane is the name of a group of clay-size minerals with short-range order which contain silica, alumina, and water in chemical combination." Halloysite is also common in volcanic areas, as are various types of the layer silicate clay minerals, depending on the degree of weathering (Dahlgren et al., 1993). Aluminum- and iron-humus complexes are also

formed in Andisols and, together with the clay constituents, give the soils their peculiar characteristics, referred to as "andic soil properties."

Soils made of relatively fresh volcanic deposits are quite different from other soils dominated by conventional parent materials such as limestone, granite, or loess sediments. The tephra is often porous and weathers rapidly if given favorable weathering conditions (e.g., Dahlgren et al., 1999, 2004; Shoji et al., 1993b). Basaltic volcanic surfaces have some of the most rapid chemical denudation rates measured, such as in Iceland (e.g., Gislason, 2008; Gislason et al., 1996). There is a provision for relatively non-weathered tephra under the Andisol soil order, if volcanic glass is dominant and the formation of colloidal matter or metal-humus complexes (MHC), indicated by oxalate soluble Al and Fe, has reached a minimum level of 0.4% $(Al+½Fe)_{ox}$ (Soil Survey Staff, 1999). These conditions are met almost immediately after deposition of basaltic tephra in Iceland (Arnalds and Kimble, 2001), but much of rhyolitic (silicic) tephra from the few thousand years old Santorini (Greece) eruption is still considered non-weathered Entisol (Quantin and Spaargaren, 2007). Due to the special properties of tephra materials, young and relatively non-weathered deposits have also been considered a special soil class: Vitrisols in France (INRA, 1998) and Iceland (Arnalds, 2008; Arnalds and Oskarsson, 2009) and Pumice soils in New Zealand (Hewitt, 1998).

Volcanic soils are often separated into two main classes based on the type of dominant colloidal constituents, allophanic- ("silandic") and MHC ("aluandic")-dominated Andisols (see Dahlgren et al., 2004). For the sake of this discussion, one more main class is added, "vitric", representing the newly deposited or non-weathered volcanic materials.

Figure 6.5 presents a simplified schematic drawing for weathering of volcanic deposits. More silicic materials tend to lead to acidifying processes and the formation of MHC-dominated Andisols, while weathering of basaltic materials initially releases cations such as Ca^{++} which maintains relatively higher pH, and resulting in the formation of allophane (e.g., Dahlgren et al., 2004; Shoji et al., 1982). Allophane formation is inhibited at lower pH than 4.9 (Shoji et al., 1993b). Formation of other minerals is not considered in this graph for the sake of simplicity. The soil development is dependent on the weathering intensity (rainfall, temperature, etc.), which is also represented on the left–right axis. Dryer conditions tend to slow weathering, especially of silicic tephra, with soils remaining as Entisols or vitric Andisol under the Soil Taxonomy (Ugolini and Dahlgren, 2002). Dryer conditions also tend to maintain higher pH. It should be noted that

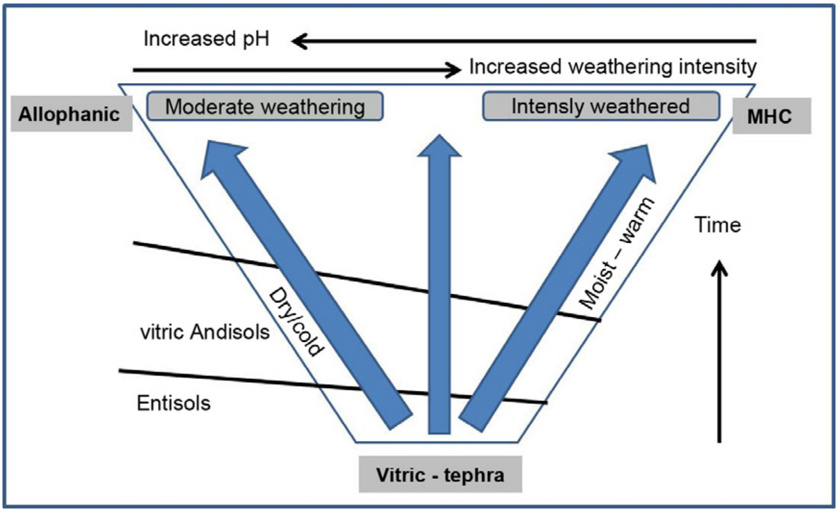

Figure 6.5 Simplified schematic drawing for weathering of recent volcanic deposits (e.g., <2000 years). Soil classes according to Soil Taxonomy. Soils become more and more allophanic or metal–humus complex (MHC) dominated as they approach respective corners and with further development become other soil types (Vertisols, Spodosols, Mollisols, Alfisols, Ultisols, etc.).

the weathering of basaltic deposits is generally more rapid than weathering of silicic materials (e.g., Kirkman and McHardy, 1980; McDaniel et al., 2011). In Iceland, it is quite evident that the silicic volcanic deposits are little weathered while the basaltic ones can reach more advanced stage of weathering after few thousand years (Arnalds et al., 1995; Stoops et al., 2008). Andisols are not stable over long periods (e.g., >10–20,000 years), and weathering continues to other soils types (e.g., Shoji et al., 1993b; Ugolini and Dahlgren, 2002). With repeated volcanic activity, new materials are added to the surface within active regions, maintaining the Andisol surface.

Soil development in volcanic deposits reflects thicknesses and the frequency of volcanic eruptions. Each eruption creates a separate layer of parent material resulting in the characteristic layered profiles, ranging from few thick tephra layers close to volcanoes, which is typical of New Zealand, to numerous thin tephra layers that have accumulated in Iceland over the past 9000 years during Holocene (see McDaniel et al., 2011). The time between tephra deposition events also determines the degree of weathering attained before the next layer is deposited on top, leading to sequences of buried genetic soil horizons.

Thick coarse tephra layers can be nonconductive to capillary rise of water in the soil, thus having an effect on water availability in the root zone. This is witnessed in Iceland (Arnalds, 2008) and also noted by Hotes et al. (2010) for wetland communities in Japan. Ecosystems with deep-rooted plants, such as trees, cutting through the coarse layers, are therefore likely to be more resilient to deposition of coarse tephra in the long term than shallow-rooted systems. The individual tephra layers can form induraded horizons and hard pans with time, which greatly affect agricultural potential and ecosystem services (Shoji and Takahashi, 2002), such as the "tepetates" in Mexico (Servenay and Prat, 2003) and hard pans in the Azores (Pinheiro et al., 2004).

5.3. Carbon cycle considerations

One of the major characteristic of soils that develop in volcanic ejecta is the accumulation of organic materials. The accumulation is both related to the mineral constituents such as allophane, often stabilizing at about 6% C in allophanic soils, and as MHC with even higher C contents (Nanzyo et al., 1993; see also Chevallier et al., 2010; Dahlgren et al., 2004; Parfitt, 2009). Andisols store more carbon reserves per unit area than other dryland soils, often >30 kg C m^{-2} (Batjes, 1996; Eswaran et al., 1993). Only organic wetland soils, Histosols, store more (Eswaran et al., 1993). Burial of organic soils by volcanic deposition is likely to aid in carbon accumulation from the atmosphere, as do steady aeolian additions of volcanic materials from unstable volcanic sediment areas, such as in Iceland (Arnalds et al., 2013a; Gisladottir et al., 2010). Overexploitation of volcanic soils does, on the other hand, contribute to greenhouse gases by releasing CO_2 into the atmosphere from the soil organic carbon pool (Shoji and Takahashi, 2002).

Lal (2004, 2008) reported common values for carbon accumulation in soils, in general, related to management improvement and restoration in the range of 0.01–0.05 kg C m^{-2} $year^{-1}$. Zehetner (2010) suggested accumulation of 0.01 kg C m^{-2} $year^{-1}$ for the world's volcanic soils after the first 1000 years with 0.03–0.06 kg C m^{-2} $year^{-1}$ in more recent soils (<200 years) based on 53 profiles from 20 published studies. Ritter (2007) reported 0.023 kg C m^{-2} $year^{-1}$ for accumulation of carbon in soils following tree plantation in degraded heathland in Iceland, and Arnalds et al. (2013a) report rates up to 0.08 kg C m^{-2} $year^{-1}$ following restoration efforts on barren volcanic deposits in Iceland, which can be maintained >100 years. Gisladottir et al. (2010) found long-term carbon accumulation in Southwest Iceland of 0.017–0.030 kg C m^{-2} $year^{-1}$, but Pena-Ramirez

et al. (2009) showed 0.0043 kg C m^{-2} $year^{-1}$ over millennia under natural conditions in Mexico. These numbers indicate high but variable carbon accumulation potential of volcanic deposits and soils. Zehetner (2010) concluded that the higher limit for carbon accumulation in Andisols was about 20 Tg $year^{-1}$, which is at most 25% of the annual C released from volcanoes.

5.4. Nutrient recharge by volcanic additions

In Section 4, it is noted that traces of volcanic materials are distributed over large areas, both oceans and terrestrial surfaces. These additions are repeated periodically close to active volcanic areas. Pelzer et al. (2010) argued that rejuvenation with nutrient rich materials is needed to prevent ecosystem retrogression. Volcanic additions; however, small in non-volcanic areas, are important on a global scale in adding fresh materials to soil systems (Nriagu, 1980), continuously and over long time (1000s of years). Vitousek et al. (2003) noted that accumulated volcanic ash can increase the fertility of relatively old tropical soils and noted that statements on the age and fertility of soils must consider erosion and accumulation factors. Calabrese et al. (2011) concluded that distribution of volcanogenic trace elements from Mt. Etna (Italy) may have a regional and global impact, with the major impact within about 10 km of the volcano. Cronin et al. (1998) reported beneficial additions of S, Se, K, and Mg in the 1995–1996 eruptions of Ruapehu in New Zealand. Volcanic ash have been suggested to have a significant impact on ocean surface waters, releasing bioavailable materials that benefit primary production (e.g., Duggen et al., 2007, 2010; Frogner et al., 2001; Jones and Gislason, 2008; Langmann et al., 2010).

6. INFLUENCE ON AGRICULTURE AND OTHER EFFECTS

6.1. Agriculture

Deposition of tephra has long-lasting impact on agriculture in the vicinity of volcanoes: on croplands, pastures, horticulture, and livestock health (Blong, 1984). Volcanic areas are often densely populated with fertile soils and diverse agriculture. There are several accounts of impacts of volcanic ash on agriculture in the literature and the USGS maintains a Web site on effects on agriculture and possible mitigation measures against negative effects of volcanic impacts (USGS Ash Web Team, 2012).

The 1980 Mount St. Helens eruption is estimated to have caused 7% reduction in crop production in the affected area the first year, with negative

impacts on hay pastures as well (Cook et al., 1981). Rees (1979) reported on the impact of the Paricutin eruption (Mexico) during the 1940s and 1950s on agriculture, which resulted in the death of >4500 cattle, 500 horses, and an unknown number of sheep due to breathing of volcanic ash. About 1000 km^2 of agricultural land was seriously affected by tephra deposition during the 1991 Mt. Pinatubo eruption (reviewed by Wilson et al., 2011a). The impact of the large (4.3 km^3 tephra) 1991 eruption of Hudson volcano in Chile (Wilson et al., 2011a) had wide ranging effects with about one million livestock killed after the eruption, together with severe effects on croplands and horticulture. The subsequent dust storms (Wilson et al., 2011b) were discussed in Section 4.

Fluoride bound to tephra surfaces is highly soluble, and its potential amount increases with decreased particle size of the tephra (Oskarsson, 1980). However, F-levels on the surface are reduced quickly with rainwater. Fluoride is often cited as a threat to livestock or even humans. Harmful effects were reported after the eruption in Popcatepetl volcano in Mexico (Armienta et al., 2011) and Mount Hekla in Iceland (e.g., Oskarsson, 1980; Thorarinsson, 1979), where 7–8000 sheep were killed after a relatively small eruption in 1970 that distributed fine-grained ash over extensive areas. Other examples include Ruapehu volcano in New Zealand where several thousand sheep were killed in the 1995 eruption (Cronin et al., 2003). The amount of fluoride release and the harmful effects vary among volcanoes, for example, in Iceland with Mount Hekla commonly being harmful but ash from the neighboring Katla volcano is not known for fluoride toxicity (Thorarinsson, 1979). Some volcanic eruptions have emitted enormous amounts of HF gases together with a range of other gases, such as the 1783 Laki eruption that affected climate, agriculture, and human health in Northern Europe (Thordarson and Self, 2003; see also Williams-Jones and Rymer, 2000). It should, however, be noted that Andisols are a strong adsorbent of fluoride, resulting in an effective immobilization of F when it is leached into the soil (Delmelle et al., 2003).

6.2. Other effects

So far, this chapter has mainly dealt with impacts of volcanic tephra on vegetation and soils. There are numerous other ecosystem components affected by volcanic ash deposition, which will not be reviewed in detail here. However, some of these are mentioned below with relevant literature. The comprehensive studies of ecological responses to the 1980 Mount St. Helens

eruption (Dale et al., 2005a) provide good comparisons to other volcanic disturbances and further references. Such holistic approach has also been taken by multidisciplinary baseline research after the 2008 eruption of the Kasatochi Island (see DeGange et al., 2010). The multidisciplinary research following ecosystem development on the Surtsey volcanic island (Iceland) formed in a 1963–1966 eruption is also noteworthy (e.g., Magnusson et al., 2009; Sigurdsson and Magnusson, 2010).

6.2.1 Streams

Stream ecosystems are affected by tephra deposition, which can change the bottom characteristics and affect flow and nutrient dynamics in the streams. Effect of game fish populations of the Mount St. Helens were reviewed by Lucas (1986) which showed severe impacts on anadromous fish populations, with burial of stream channels and raising water temperatures, and eliminating organic debris, but recovery was partly well under way few years later. Gamblin et al. (1986) investigated area impacted by about 2 cm tephra from the Mount St. Helens deposition where it had limited and temporary impact.

6.2.2 Insects

The influence of tephra on insects, like other components of the ecosystem, depends on the amount and nature of the tephra deposits, and the pre-burial ecosystem. Adams and Leffler (1986) found that distance from source of immigration, soil moisture, and texture were key factors for recolonization insects within the blast zone of the 1980 Mount St. Helens eruption. Sugg (1986) showed that recovery processes of arthropods after the Mount St. Helens eruption were sensitive to depth of tephra deposited and vegetation emergence after the impact and conditions prior to the eruption. Edwards et al. (1986) noted that the formation of desert pavement surface and suitable microtopography for shelter is a prerequisite for permanent arthropod populations in blast zones (pyroclastic flows). Sikes and Slowik (2010) investigated the initial impact of the 2008 Kasatochi Island (Alaska) on terrestrial arthropods, noting a shift from plant-based to necromass-based foot web.

6.2.3 Animals

Fluor toxicity will affect wild animals as the livestock, but tephra also has an effect on grazing grounds, ground holes, and bird nesting places (e.g., Williams et al., 2010). Mobility of animals is important and the availability

of other less impacted habitats. Adams et al. (1986a) showed that small mammals returned to the Mount St. Helens severely impacted zones within years utilizing a diversity of the ecosystem remnants after the impact and elements of the recovering system. Merrill et al. (1986) described the mortality and recolonization of Elks in the Mount St. Helens impact zone. Crisafulli et al. (2005) discussed the survival of small mammals after the Mount St. Helens eruption, including within the tephra deposition zone. They state that survival was greater than initially expected, and it was inversely related to disturbance intensity.

7. CONCLUSIONS

Volcanic eruptions affect a large proportion of Earth's ecosystems to some degree, both on land and sea (Sections 1 and 5). Soils that develop in materials dominated by volcanic ash acquire unique properties that separate them from other soil types (Section 5). These soils, termed Andisols, are often fertile soils and sustain high population densities in volcanic areas but cover only about 1% of Earth's land. The magnitude of volcanic ash impacts on regional and global scale is often poorly accounted for. Rose and Durant (2012) pointed out the need to monitor global ash deposition, especially for the fine ash particles, which can remain airborne for weeks.

The study of volcanic impacts, with their diverse nature, complexity of the affected systems, and the multiple pathways of recovery, calls for multidisciplinary approaches involving geologists, ecologists, soil scientists, geomorphologists, and practitioners other disciplines. Ecosystem recovery may take from few years to 1000s of years, involving complex interaction of ecosystem components which requires long-term research and monitoring (del Moral, 2010; Svavarsdottir and Walker, 2009).

The reviewed literature clearly demonstrates that the impact of tephra deposition is largely determined by the interaction between vegetation height and the depth of the tephra (Fig. 6.3), while other factors such as the nature of the ecosystem impacted, tephra, and surface roughness are also important (Section 3). Arctic, alpine, and desert environments with low or discontinuous vegetation are more susceptible to tephra impacts and subsequent soil erosion than areas with taller vegetation, such as forested areas. This is exemplified by Iceland, where birch forests can tolerate over 20 cm of tephra while low growing Arctic vegetation is severely damaged by few centimeter-thick deposits (Section 3). Surface roughness affects subsequent erosion processes and redistribution of tephra (Section 4).

Ecosystem resilience is a major factor influencing ecosystem responses, with ecosystems subjected to heavy grazing and intense agricultural practices more vulnerable to volcanic disturbance and redistribution of volcanic materials than more lush rangelands and forests (Section 3). The interaction between repeated volcanic events and land use practices can also be detrimental, as shown in Iceland and where clear-cutting practices interfere with recovery on the slopes of Mount Usu. Alien plant species in volcanic areas can also severely interfere with ecosystem recovery.

Erosion processes and redistribution of volcanic tephra are major elements of volcanic impacts, prolonging the influence of eruptions and sometimes having devastating consequences such as lahars. The effects can, however, be locally positive as removal of tephra can aid recovery and where tephra materials are redistributed over hard lava and pyroclastic flow surfaces (Section 4). While values for average tephra deposition thicknesses are often reported, the redistribution of volcanic materials in the aftermath of eruptions can reduce the thicknesses, especially when the tephra is thicker than the vegetation adsorbing the impact. Redistribution of tephra by water has received considerable attention, but wind erosion can also have severe consequences as exemplified by the 1991 Hudson eruption in Chile. Iceland is continuously subjected to wind erosion of volcanic materials, affecting ecosystems on land, oceanic systems, and air quality (Section 4.2).

Volcanic eruptions are spectacular events that draw a lot of attention and research efforts in geosciences, commonly with papers published in the highest impact journals soon after the events. The aftermath of volcanic eruptions, with continuous erosion and flood threats and continued harmful effects on ecosystems and humans have not received as high-profile attention or research efforts, yet may cause more impact on ecosystems and society than the original events.

ACKNOWLEDGMENTS

The author is grateful to Asa L. Aradottir, Margret Jonsdottir, and Gudrun Thordardottir for all their help in preparing this chapter.

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CHAPTER SEVEN

Advances in Elucidating Beneficial Interactions Between Plants, Soil, and Bacteria

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Contents

Abstract

Survival of every organism on earth depends on its interactions with other organisms. For example, animals form associations with the intestinal microflora, while plants develop symbiotic associations with neighboring plants, microflora, and microfauna. Most of the associations between plants and microorganisms are mediated by organic compounds released by the plant. The plant root system acts as a factory and exudes enormous amount of chemicals to effectively communicate with the surrounding soil organisms. Bacteria on roots and in the rhizosphere can also utilize these organic compounds as a source of nutrients and enhance their population size and metabolic activities. In return, plant-associated bacteria improve plant growth and development by

Advances in Agronomy, Volume 121
ISSN 0065-2113
http://dx.doi.org/10.1016/B978-0-12-407685-3.00007-4

different mechanisms including nitrogen fixation, provision of nutrients, and mediating resistance against pathogens. Although plant–bacterial partnerships have been found effective to enhance biomass production, their importance and relevance in agricultural systems are still underestimated. A better understanding of beneficial interactions between plant, soil, and bacteria could be exploited to improve growth and health of food and feed crops. Plant growth-promoting mechanisms of bacteria might enhance biomass production in a more sustainable manner, even on marginal land. Furthermore, plant growth-promoting and/or pollutant-degrading activities of bacteria could be exploited to improve the efficiency of phytoremediation of organic and inorganic pollutants from the soil and water or to protect the food chain by decreasing the concentrations of pollutants in food crops.

1. INTRODUCTION

As autotrophic organisms, plants play a major role in sustaining all other life forms. The plant root system is a chemical factory that mediates several interactions of the plant with soil microorganisms. Roots release organic compounds, which act as signaling agents to attract beneficial microbes and to combat pathogenic ones. Generally, these interactions are mutualistic with beneficial microbes, such as rhizobia, mycorrhizae, endophytes, and plant growth-promoting rhizobacteria (PGPR). However, these plant–microbe interactions are not only driven by organic compounds released by the roots but are highly integrated with and influenced by biotic and abiotic factors (Lichtenthaler, 1998; Phillips et al., 2004). Root-released organic compounds also enhance the abundance and diversity of beneficial microorganisms in the rhizosphere and plant environment. In return, plant-associated microbes may enhance plant growth and health by several activities such as nitrogen fixation, synthesis of plant hormones and vitamins, the improvement of nutrient uptake, and induction of stress resistance. They also outcompete invading pathogens by different mechanisms such as niche occupation by competition for space, nutrients, and physical niches of the rhizosphere/rhizoplane and endophytic tissues. Some of the beneficial rhizo- and endophytic bacteria can secrete not only antibiotics but also lytic enzymes enabling the inhibition of various pathogens (Pleban et al., 1997). Plant–microbe interactions are affected by many different regulatory signals, of which only few have been explored, recalling a quote by Leonardo da Vinci saying that “We know better the mechanisms of celestial bodies than the functioning of the soil below our feet” (Badri et al., 2009).

Most of the plant-associated bacteria are also soil inhabitants (Rasche et al., 2006a,b). They may move from the bulk soil to the rhizosphere of the living plant and aggressively colonize the rhizosphere and roots of plants. Some of them can penetrate plant roots, and some strains may move to shoots, leaves, flowers, and even seeds (Compant et al., 2010a; Reinhold-Hurek and Hurek, 2011). However, different plant species host different microbial communities (Berg and Smalla, 2009), which is mostly due to the different composition of root exudates excreted by different plants. Root exudates play an important role in signaling and developing microbial communities in different compartments of plants.

Plant growth-promoting mechanisms differ between bacterial strains and to a great extent depend on the type of organic compounds released by these strains. For example, plant growth-promoting hormones and other secondary metabolites released by the bacteria can alter plant growth and development. Recently, it has been reported that associations between plant and associated bacteria have reached such levels that the host plant cannot develop properly without their associated bacteria (Carlier and Eberl, 2012). In addition to sustainable growth of food and feed crops, bacteria may enhance plant growth and the remediation of organic and inorganic pollutants from the soil and water. The enhanced microbial population in the rhizosphere can mineralize organic contaminants in the soil. In case of inorganic pollutants, microorganisms enhance the uptake of heavy metals and other inorganic pollutants from the soil. In this regard, interactions among plant, soil, and bacteria have received great attention because of the biotechnological potential of microorganisms for improving growth of food and feed crops and the remediation of pollutants from the contaminated environment.

Although many studies showed that plant-associated microbes have beneficial effects on their host, their importance during plant growth and development is still underestimated. A better knowledge of the interactions between plant, soil, and bacteria could be made applicable for higher yields of food and feed crops, and to improve phytoremediation of contaminated soil and water. In this review, we describe beneficial interactions between plant, soil, and bacteria and how these can be exploited in agriculture as biofertilizers, growth stimulants, or biopesticides replacing chemical pesticides or fertilizers supporting a sustainable use of natural resources. Furthermore, plant-associated bacteria that possess pollutant-degrading and/or plant growth-promoting activities can assist in remediating marginal lands polluted by organic pollutants and/or toxic metals, in addition to improving biomass production.

2. MICROBIAL HABITATS IN RELATION TO PLANT–SOIL–MICROBE INTERACTIONS

Plants consist of a rich habitat for microbial life. They do not only act as source of energy, but provide bacteria with specific niches, where they can thrive and multiply. The association of bacteria with plants reaches from a loose connection of leaf epiphytic and root-associated bacteria to bacteria living in intercellular spaces as pathogens or as commensal or beneficial endophytes to highly adapted organisms capable of inhabiting the intracellular spaces, again as pathogens, commensialists, or endosymbionts (Reinhold-Hurek and Hurek, 2011; Ryan et al., 2008). In the commensal situation, the environment in or at the plant provides a niche for bacterial life benefitting the bacteria, but the interaction has no known effect on the plant host (Newton et al., 2010), though this situation might simply reflect our limited knowledge on the function of plant-associated bacteria in nature. Pathogens and commensal endophytic bacteria share very similar habitats in the plants, which makes them good potential candidates for biocontrol, as they can compete with pathogens for niches in or next to the plant and are in close physical connection with plant pathogens (Ryan et al., 2008).

The root surfaces and their surroundings, the rhizosphere, are inhabited with up to a concentration of 10^{10} bacteria per gram, due to the existence of nutrient-rich root exudates and corresponding niches (Lynch, 1990). This concentration is clearly higher than in nonrooted bulk soil. Bacteria on roots and in the rhizosphere can benefit from these root exudates, and both beneficial bacteria and plant pathogens can densely inhabit root surfaces, thereby forming organized biofilms with complex organization and high persistence capability (Ramey et al., 2004). A subset of the rhizosphere microflora may also enter the plant as endophytes, which, by definition, do not harm the host plant, but form commensal or mutualistic communities with plants (Rosenblueth and Martinez-Romero, 2006). Bacteria can enter plant tissues at root hairs, elongation zones, root tips, and at emergence sites of secondary roots and then colonize areas of lysed plant cells and intracellular spaces, and less frequently, also xylem cells and vascular tissues (Compant et al., 2010a; Reinhold-Hurek and Hurek, 2011). The invasion of plant cell tissue may require the production of lytic enzymes facilitating the colonization process. Alternatively but less frequently documented points of entry of endophytes include above-ground natural openings such as stomata, wounds created

by herbivore feeding, and occasionally documented transfer to the next generation in seeds. Niche occupation within the plant can be very similar to plant pathogens and indeed certain strains of bacteria can form devastating pathogens, while very closely related species or even strains inhabiting a similar plant niche are harmless or even protective. This is, for example, the case for the causal agent of Pierce disease of grapevine, *Xylella fastidiosa*, where specific strains cause a devastating disease, while others can be harmless or even act as beneficial biocontrol agents (Hopkins, 2005).

The plant colonization processes of endophytes have been visualized by autofluorescent proteins convincingly demonstrating the colonization of wide range of vascular plants by endophytic bacteria (Rosenblueth and Martinez-Romero, 2006; Ryan et al., 2008). Endophyte concentration in plants is considerably lower than in the surrounding rhizosphere, and concentrations generally decrease in upper parts up to the reproductive organs. Nevertheless, certain endophytes are capable of colonizing even the reproductive tissue and even seeds, as demonstrated for *Burkholderia phytofirmans* PsJN and other endophytes in grapevine (Compant et al., 2008a, 2011). Colonization pattern of beneficial bacteria might also depend on the host plant (Sessitsch et al., 2005). While root hairs are generally favored by *Bacillus amyloliquefaciens* FZB42 in both maize and *Arabidopsis*, this bacterium colonizes tips of primary roots in *Arabidopsis*, but not in maize (Fan et al., 2012). The colonization of the leguminous tree *Robinia pseudoacacia* by the endophytic *Bacillus subtilis* strain GXJM08 starting at root hairs is even accompanied with morphological changes of the root hairs (Huang et al., 2011).

In legumes, a highly specialized endosymbiotic relationship with rhizobia (mostly *Proteobacteria*, *Rhizobiales*) has evolved. This relationship results in the formation of special organs, root nodules, on the roots of the host plants. There, nitrogen fixation occurs supporting the host plants with nitrogen, while the rhizobia are accommodated intracellularly in nodule cells and are supplied with carbon sources by the plant. This close relationship has been investigated intensively, also at the molecular level, and has been recently reviewed by Murray (2011). In addition, recently, various *Burkholderia* strains have been shown to form nodules on legumes like rhizobia (reviewed in Compant et al., 2008b). Other nodule-forming, nitrogen-fixing bacteria belong to the genus *Frankia* (*Actinobacteria*), where nodule formation occurs in roots of different plant species in the orders Cucurbitales, Fabales, and Rosales. The nodule structure of this actinorhizal symbiosis is different from rhizobia–legume nodules and has been reviewed very recently by Pawlowski and Demchenko (2012).

In addition, specific bacteria of the genus *Burkholderia* such as *B. kirkii* have specialized in their adaption to the endophytic life within plants so far that they inhabit specific leaf nodules and are transmitted vertically. The dependency has reached such levels that the host plant (*Psychotria* spp., *Rubiaceae*) cannot develop properly without these symbiotic bacteria. Interestingly, as the genome sequence suggests, these nodule bacteria do not seem to benefit the host plant in nitrogen fixation, but may function as producers of secondary metabolites, thereby protecting the host plant against herbivores or pathogens (Carlier and Eberl, 2012).

3. ECOLOGY OF PLANT-ASSOCIATED BACTERIAL COMMUNITIES

3.1. Diversity of plant-associated bacterial communities

Due to the availability of root exudates and decayed plant cells providing important nutrients, the rhizosphere is known as a hot spot of microbial activity (Lynch, 1990). This microenvironment supports also high bacterial abundance of approximately 10^{10} bacterial cells per gram rhizosphere soil, which is generally one or two magnitudes higher than bacterial abundance in bulk soil. Rhizosphere microorganisms have a major force on plant performance, that is, plant growth and health, as they can be pathogenic, beneficial, or neutral (Lynch, 1990).

Numerous studies have revealed the presence of a tremendous diversity in the rhizosphere comprising thousands of bacterial species. By cultivation, copiotrophs (i.e., *r* strategists) as well as oligotrophs (i.e., *K* strategists) have been found in the rhizosphere, but they have been reported to occupy different niches (Semenov et al., 1999). Niches providing high nutrient availability including zones of root exudation such as root hairs will be colonized rather by *r* strategists, whereas nutrient-poor or -depleted niches will tend to be colonized by *K* strategists (Semenov et al., 1999). For many years, cultivation-based methods were used to assess the diversity and richness of bacteria colonizing the rhizosphere revealing the presence of many different Gram-negative and Gram-positive bacteria. Famous representatives include *Pseudomonas*, *Burkholderia*, *Azospirillum*, and many more *Proteobacteria*, *Firmicutes* comprising mostly *Bacillus* and *Paenibacillus* as well as *Actinobacteria* such as *Streptomyces*. Many of these isolates have been further tested for plant growth-promoting and other activities and their functional capacities are discussed below.

Since the application of cultivation-independent analysis approaches, we have obtained a far better understanding on the diversity and ecology of microbial communities in general. Due to the fact that still many bacteria are unknown or have not been isolated yet, we do not know yet how to cultivate the huge diversity of prokaryotes. Furthermore, bacteria can enter a viable-but-nonculturable state depending on environmental conditions (Vriezen et al., 2012). The use of specific cultivation conditions introduces also a bias as a subset of the bacterial richness is able to grow under specific conditions or on a particular growth medium, whereas other bacterial fractions need different cultivation conditions. However, instead of cultivating and isolating bacteria, whole community DNA can be isolated and subjected to a diversity analysis. This is achieved by the use of phylogenetic markers such as the 16S rRNA gene, which are amplified by PCR and further analyzed by community fingerprinting methods including denaturating gradient gel electrophoresis or terminal restriction fragment length polymorphism analysis, pyrosequencing, ion torrent technology, sequence analysis as well as by other tools including microarray analysis or hybridization. Sequence analysis in particular has revealed a huge bacterial diversity in the rhizosphere as well as in many other environments, and many new taxa have been identified. In the rhizosphere, *Proteobacteria* have been generally identified as the dominant bacterial phylum (Buée et al., 2009), which is generally in agreement with cultivation-based analysis. Several prominent plant growth-promoting genera belong to this phylum such as nitrogen-fixing and symbiotic *Beta*- and *Alphaproteobacteria* including many different genera (e.g., *Rhizobium*, *Bradyrhizobium*, *Sinorhizobium*, *Burkholderia*, *Cupravidius*) and species. Additional well-known representatives include *Azospirillum*, which has found agricultural application as phytostimulators, biofertilizers (Hungria et al., 2010), or *Pseudomonas* comprising strains with plant growth promotion or biocontrol activities (van Loon et al., 1998) but also some other genera as outlined later in this chapter. Nevertheless, even the phylum *Proteobacteria*, which is considered to be culturable, comprises many novel taxa and intraspecific diversity assessment may lead to different findings when analyzed by cultivation-dependent or -independent analysis. Molecular methods revealed that taxa, which have been rarely cultivated so far and for which very limited information is available, seem to play an important role in the plant environment as well. Sophisticated approaches such as pyrosequencing or microarray analysis of 16S rRNA genes revealed the presence of *Acidobacteria*, TM7, *Verrucomicrobia*, and *Chloroflexi* in the rhizosphere or inside roots

(Manter et al., 2010; Sessitsch et al., 2012; Weinert et al., 2010). In addition, by applying other cultivation-independent approaches targeting the 16S rRNA gene have identified these taxa as well, although their occurrence seems to be variable and certain subgroups seem to be particularly encountered in the rhizosphere (da Rocha et al., 2009). In particular, *Acidobacteria*, which are usually very abundant in soils, but hardly culturable, have been found in the rhizosphere in highly varying numbers (Buée et al., 2009). Information regarding functional characteristics or the interaction with plants is very limited; however, it has been recently reported that *Acidobacteria* respond to root exudates (Vandenkoornhuyse et al., 2007). da Rocha et al. (2009) suggested novel cultivation approaches targeting rarely cultivated taxa such as *Acidobacteria* or *Verrucomicrobia*, which would enable further functional analyses and better understanding on their functional role in the plant environment. Other taxa including *Actinobacteria*, *Firmicutes*, or *Bacteroidetes* are commonly found in the rhizosphere, but in variable abundance. Still a quite high percentage of bacterial 16S rRNA genes encountered in the rhizosphere belong to yet-unclassified taxa (Buée et al., 2009). Inceoglu et al. (2011) found by pyrosequencing of 16S rRNA genes in the rhizosphere of field-grown potato plants yet-unclassified bacteria as a dominant group together with *Actinobacteria* and *Alphaproteobacteria*. Furthermore, this study showed that the community was composed of few highly dominant species together with numerous rare species.

Apart from the interactions of plants with soil bacteria, plants may host also bacterial communities inside the plant. A well-known endosymbiotic, beneficial interaction is between legumes and rhizobia, in which the microsymbionts live in specific plant structures, so-called nodules, and are thereby entrapped and surrounded by a host membrane. Unlike endosymbionts, endophytic bacteria generally do not colonize intracellular spaces but colonize vascular tissues and intercellular spaces. Endophytes have been defined as microorganisms, which live inside plants but do not do any harm to their hosts (Wilson et al., 1995). Different definitions can be found, however, in the literature (see, for instance, the ones of Stone et al., 2000; Kobasyashi and Plumbo, 2000). Although already in 1887, Galippe postulated that bacteria can colonize plants internally; for a long time, it was believed that only phytopathogens can enter the plant and colonize internally (Compant et al., 2012). This work was followed by studies of Jorissen, Marcado, and some other criticized and forgotten scientists. However, nowadays it is clear that endophytic bacteria mostly derive from the rhizosphere environment (Compant et al., 2005; Hardoim et al., 2008; Sessitsch et al., 2002a).

Although other sources can also be the carposphere, anthosphere, laimosphere, spermosphere, as well as the caulosphere, numerous studies have shown that endophytic communities are diverse and almost all of them are facultative (Hardoim et al., 2008). It is not completely understood how endophytes overcome plant defense reactions, but they generally colonize the rhizosphere and rhizoplane before entering plant tissues (Compant et al., 2010a). Passive penetration may occur at the root tip level and at cracks such as those occurring at root emergence sites, but generally many endophytes are equipped with cell wall-degrading enzymes, which are probably needed for efficient plant colonization and spread within plant tissues (Compant et al., 2010a; Lodewyckx et al., 2002).

As most endophytes derive from the rhizosphere, root endophytic communities are most diverse. Cultivation-based as well as -independent approaches indicate that as in the rhizosphere, *Proteobacteria* seems to be the most important phylum among bacterial endophytes, comprising a range of different *Alpha*-, *Beta*-, and *Gammaproteobacteria* (Berg et al., 2005; Sessitsch et al., 2012). However, different intraspecific diversity of rhizosphere and endophytic bacterial communities have been reported, indicating that different strains belonging to the same genus or species are adapted to live in the rhizosphere or endosphere (Idris et al., 2004). Furthermore, even within the *Proteobacteria*, different taxa are found in both environments. *Enterobacteriaceae*, for example, comprising *Pantoea* and *Enterobacter* have been found as frequent endophytic plant colonizers (Holden et al., 2009; Montañez et al., 2009; Yousaf et al., 2011), but are far less frequently found in the rhizosphere. Even human pathogenic members of the *Enterobacteriaceae* including *Salmonella* and *Escherichia coli* have been repeatedly reported as endophytes (Holden et al., 2009). In addition to *Proteobacteria*, Gram-positive taxa occur as endophytes and seem to be very important in some plant environments (Francis et al., 2009). Both *Firmicutes* (e.g., *Bacillus*) and *Actinobacteria* (e.g., *Streptomyces*) are well known for their ability to produce antibiotics and other secondary metabolites, and they became particularly interesting for biotechnological applications and bioprospection (Qin et al., 2011).

3.2. Interplay between soil, plant, and environment in shaping plant-associated microbial communities

Microbial communities, including rhizosphere and endophytic assemblages, are highly complex and their structure as well as their functioning strongly depends on environmental parameters. They rapidly sense nutrient conditions as well as certain stress factors influencing the survival and competitiveness of

individual community members leading to community shifts under altered conditions. Such altered communities may also mediate different functional activities. Alternatively, different environmental conditions may directly affect microbial communities (e.g., by altering gene regulation), which will not only influence functioning, but may on the longer term also result in community shifts. The most important drivers regarding the structure of plant-associated microbial communities are the soil, the plant, and other environmental parameters. Soils themselves host distinct microorganisms serving as reservoir for rhizosphere as well as the endosphere bacteria (Rasche et al., 2006a,b). Soil type, structure, pH, water content as well as other factors shape soil microbial communities. Therefore, the same plant growing in different soils or soil types will be colonized by different strains; however, at the genus or species level, similar species might colonize, depending on the kind of microorganisms prevalent in a particular soil.

3.2.1 The plant host structures plant-associated microbial communities

The plant host is a very important driver of plant-associated microbial communities, in both the rhizo- and endosphere (reviewed by Berg and Smalla, 2009). The root type might affect microbial communities (Garbeva et al., 2004) as roots alter soil structure, water flow, or oxygen availability and therefore are also likely to influence soil microbiology. Furthermore, it is well known that different plant species host different microbial communities (Berg and Smalla, 2009), which is very likely due to different root exudation patterns attracting different types of bacteria. Plant host specificity is not fully understood, but root exudate composition and abundance differ from plant to plant and therefore seem to provide a specific nutrient composition attracting specific microorganisms. Low molecular weight carbon compounds including sugars, organic acids, and amino acids are prominent root exudates and are readily assimilated by soil microorganisms. They have been proposed to be an important driver of microbial community structuring in the rhizosphere (Bais et al., 2006; Baudoin et al., 2003; Weissknopf et al., 2008). The influence of root exudate fractions or compounds on microbial community structures has been assessed (Henry et al., 2008; Paterson et al., 2007; Shi et al., 2011), confirming that root exudates play a primary role for regulating the formation of rhizosphere microbial communities. Root exudates might not only serve as nutrient but may also contain certain signal molecules supporting the interaction with the plant. The cross talk between legumes and rhizobial symbionts (reviewed by Cooper, 2007) is well known and is initiated by flavonoids released by roots and required for the initiation

of the nodulation process by inducing rhizobial *nod* genes. A range of different flavonoid molecules are known, and the type of molecule seems to determine the specificity of the interaction. Flavonoids or mixtures of flavonoids released by roots exhibit their gene-inducing activity at micromolar or even nanomolar concentrations. Flavonoids can serve as inducers of certain rhizobial types but act as anti-inducers of others (Cooper, 2007). Consequently, by means of such signal molecules, plants can select very specifically their microsymbionts. Furthermore, plants may produce secondary metabolites such as antimicrobial compounds affecting below-ground diversity.

Different root exudate patterns determine the structure of microbial communities in the rhizosphere either generally by providing a certain environment and source of nutrients or specifically by antagonizing or interacting with specific microorganisms. As an example for the effect of the plant species on plant-associated microbial communities, Yousaf et al. (2010a) found different, host-specific hydrocarbon-degrading bacterial communities in the rhizosphere as well as the endosphere of Italian ryegrass and birdsfoot trefoil grown in the same soil. Similarly, Li et al. (2011) reported that the plant species is the main driver of microbial composition in the rhizosphere of five pioneer plants grown at a mine-tailing site. Also, agricultural plants including oilseed rape and strawberry were reported to host distinct, specific rhizosphere bacterial communities and the plant species in particular shaped *Actinobacteria* communities (Costa et al., 2006). Furthermore, seven different medicinal plants grown in Panxi, China, hosted unique actinobacterial communities (Zhao et al., 2012a).

It can be assumed that different cultivars belonging to the same genotype produce similar root exudates and therefore are likely to host similar microbial communities. Accordingly, Weinert et al. (2010) found that the diversity and structures of tuber-associated bacterial communities of different potato cultivars were nearly identical, and a cultivar effect was only found on *Pseudomonas* spp., but not on other analyzed taxa. Furthermore, an in-depth analysis by phylochip analysis of 16S rRNA genes revealed that 9% of all operational taxonomic units were cultivar specific (Weinert et al., 2011). This might be due to slight differences in plant physiology potentially resulting in slightly differing root exudation and some variations in associated microbial communities. However, such variations seem to also depend on other parameters such as the soil type or climatic factors as cultivar-specific effects are not consistently found. Experiments performed at different field sites with distinct potato cultivars revealed that cultivars generally host many common taxa and that at different sites varying

effects of the cultivar were found (Weinert et al., 2010, 2011). Rasche et al. (2006a,b) planted different potato cultivars in different soils and found strong plant genotype effects in one soil, whereas in the other soil, the different cultivars hosted very similar rhizosphere and endophytic communities. Various studies addressed potential effects of genetically modified plants on soil- and plant-associated microbial communities; however, generally only few differences were found between transgenic lines and their nearly isogenic parental lines (Gschwendtner et al., 2009; Gyamfi et al., 2002; Prischl et al., 2012; Weinert et al., 2009). Mostly, these differences were comparable to the differences found between different cultivars. Recently, Gschwendtner et al. (2009) found that rhizosphere microbial communities of two potato cultivars differed in metabolizing root-derived carbon. This was determined by incubation of plants with $^{13}CO_2$ and subsequent analysis of ^{13}C incorporated in phospholipid fatty acids (PLFAs) of bacterial communities. One cultivar incorporated higher levels of ^{13}C in PLFAs and might indicate more rapid turnover of root exudates and/or an enhanced ^{13}C:^{12}C of root exudates (Gschwendtner et al., 2009). Similarly, hybrid rice showed greater CO_2 flux and total microbial biomass, bacterial and fungal abundance, and enzymatic activities than other rice cultivars (Hussain et al., 2011). Rasche et al. (2009) used ^{13}C-labeling techniques and analyzed endophytic bacteria in two potato varieties, which were to a certain time point able to metabolize plant photosynthates. The two varieties showed different active endophytic communities, maybe due to a different timing of the photosynthesis pathway resulting different set of metabolites available for endophytes. This confirms that cultivars may show differences in rhizodeposition or plant physiology resulting in changes of microbial diversity and/or activity; however, such differences are usually small in comparison to those differences found between different plant species.

The vegetation stage has been found to greatly determine the structure of plant-associated microbial communities. Monteiro et al. (2011) studied rhizosphere and root endosphere bacterial community structures of vetiver plants at five plant growth stages. Predominant bacterial communities, both in the rhizosphere and inside roots, varied greatly with plant age. This is likely due to different root exudation patterns or metabolite profiles at different vegetation stages. Recently, Andreote et al. (2010) compared the effects of plant cultivar, developmental stage, and bacterial inoculation on the structure of potato-associated rhizosphere and endophytic bacterial communities. The developmental stage followed by the plant genotype was the main driver of community structures. However, also inoculation with plant growth-promoting

bacterial (PGPB) strains such as a *Paenibacillus* and a *Methylobacterium* influenced microbial community structures (Andreote et al., 2010). Comparative analysis of rhizosphere bacterial communities of field-grown potato plants by pyrosequencing of 16S rRNA genes again revealed different community structures at different plant growth stages (Inceoglu et al., 2011). Furthermore, a cultivar effect was only found at the young plant stage, whereas no significant differences between rhizosphere bacterial communities of different potato cultivars were found at the flowering or senescence stage.

3.2.2 Effects of environmental parameters on plant-associated microbial communities

Finally, other biotic and abiotic factors affect microbial community structure in the rhizosphere or inside plants. Biotic factors include, for instance, the presence of plant pathogens and/or the subsequent effect of a diseased plant on the plant-associated microflora. Pathogens generally induce a cascade of reactions in plants leading to the synthesis of stress metabolites including H_2O_2, phytoalexins, or stress signals such as jasmonic acid, ethylene, or salicylic acid (SA) (Lichtenthaler, 1998). Furthermore, pathogen-infected plants have shown different root exudates composition containing different amounts of sugars or organic acids (Kamilova et al., 2006; Neumann and Römheld, 2007; Phillips et al., 2004). Consequently, a pathogen-infected or diseased plant may attract and interact with different types of microorganisms due to the production of different metabolites. This was confirmed by various studies showing that diseased plants show different rhizosphere or endophytic communities. Yang et al. (2001) compared rhizosphere bacterial communities of healthy avocado trees and trees that were infected with the root-rot pathogen *Phythophthora cinnamoni*. Although plants were free of disease symptoms, they hosted different rhizosphere communities. However, trees treated with a disease-suppressive *Pseudomonas fluorescens* strain hosted comparable rhizosphere communities as healthy, noninfected plants. Similar findings were obtained with potato plants infected with *Erwinia carotovora* ssp. *atrospetica* revealing significantly different rhizosphere and endophytic communities in healthy and infected plants (Rasche et al., 2006a,b; Reiter et al., 2003). Recently, Trivedi et al. (2012) studied how *Candidatus* Liberibacter asiaticus, causing Huanglongbing disease in citrus, affects the diversity and functioning of the rhizosphere microflora. This pathogen is an obligate endophyte and caused significant changes in the rhizosphere microflora, although there is no direct interaction between the pathogen and rhizosphere bacteria. As the pathogen causes a blockage of photoassimilate transport to the roots,

the authors postulate that qualitative and quantitative changes in partitioning of photoassimilates were responsible for the observed changes. In that study, healthy plants showed a higher abundance of *Proteobacteria*, whereas *Acidobacteria*, *Actinobacteria*, and *Firmicutes* were more represented in pathogen-infected plants. Furthermore, many genes involved in key ecosystem functions such as nitrogen cycling, phosphorus utilization, or carbon fixation were more abundant in healthy than in infected plants, indicating also that important ecological processes may be impacted by alterations in the rhizosphere microflora (Trivedi et al., 2012).

Similar to biotic stress factors, abiotic stress factors such as chilling, drought, and the presence of toxic substances such as heavy metals may influence the structure of the plant-associated microflora. Various stress factors may directly influence microorganisms altering, for example, their activity and as a consequence also community structure. Furthermore, the plant will be affected by stress and respond with the production of stress metabolites and altered physiological behavior, which may result in different activity and/or diversity of associated microorganisms. Potato plants suffering from light deficiency hosted less diverse endophyte bacterial communities than healthy and robust plants (Sessitsch et al., 2002a). Similarly, chilling had a major force on the structure of endophyte communities (Rasche et al., 2006c).

Other parameters such as agricultural management or climatic conditions may affect the diversity as well as the activity of plant-associated microorganisms. Agricultural management practices such as crop rotation or the type of fertilizer applied have been reported to be important drivers of soil microbial diversity and functioning (Orr et al., 2011; Wakelin et al., 2007; Wu et al., 2008). As such also plant-associated microbes will be affected indirectly. However, they might also be directly affected, for example, due to different nutrient availabilities. It has also been reported that the agricultural management may influence plant gene expression (van Dijk et al., 2012) potentially resulting in slightly altered root exudation or metabolite profiles associated with altered microbial community structures. Various climatic factors such as temperature and precipitation are likely to affect plants and their associated microflora in many ways. Even climate change parameters such as elevated atmospheric CO_2 have been reported to affect plant microbiology (Compant et al., 2010b; Drigo et al., 2009; Nguyen et al., 2011). Drigo et al. (2010) found that arbuscular mycorrhizal fungi act as a major conduit in the transfer of carbon derived from elevated CO_2 between plants and rhizosphere bacteria again illustrating the complex interactions between plants, associated microorganisms, and the environment.

4. BENEFICIAL PLANT–MICROBE INTERACTIONS

4.1. Plant growth promotion and nutrition

In the late 1970s, Kloepper and Schroth introduced the term “PGPR” to describe bacteria that colonize plant roots after seed inoculation and that stimulate plant growth (Kloepper and Schroth, 1978). Many plant-associated bacteria—rhizosphere bacteria but also endophytes—can stimulate plant growth and nutrition (for a review, see Lugtenberg and Kamilova, 2009; Fig. 7.1). The best studied plant growth-promoting genera are *Azospirillum*, *Azotobacter*, *Bacillus*, *Burkholderia*, *Enterobacter*, *Klebsiella*, *Pantoea*, and *Pseudomonas*. Today, we observe an increasing scientific interest in bacteria with the ability to stimulate plant growth and nutrition, which is reflected in a rapidly growing number of publications on this topic. In Table 7.1, we summarized recent reports in which the molecular mechanisms underlying the plant-stimulating activity of bacteria have been identified.

So far, proposed mechanisms by which bacteria stimulate plant growth and nutrition include plant hormone production, decreasing ethylene levels, biological nitrogen fixation, and increasing the availability of nutrients such as iron or phosphate. Besides those frequently reported activities, other modes of bacterial growth promotion are discussed such as the production of volatiles, the synthesis of vitamins, and microbial photosynthetic activity or promotion of photosynthetic efficiency in plants. The plant growth-promoting activity of most PGPR or PGPB is based on the combination of two or more mechanisms. Moreover, synergistic effects of coinoculated PGPB were also reported (Chatterjee et al., 2011). Tilak et al. (2006), for example, tested dual inoculations of various PGPBs such as *Pseudomonas putida*, *P. fluorescens*, or *Bacillus cereus* strains with *Rhizobium* sp. (AR-2-2 k) and *Rhizobium* on pigeonpea and observed increased plant growth, nodulation, and improved nitrogenase activity. *Azospirillum* spp. enhanced nodulation and plant growth of common bean (*Phaseolus vulgaris* L.) when coinoculated with *Rhizobium* in a plant genotype-dependent manner (Remans et al., 2008).

4.1.1 Biological nitrogen fixation

Plant-associated microorganisms may play an important role for plant nutrition. One of the most prominent mechanisms is biological nitrogen fixation, which was discovered by Beijerinck (1901) and is a process in which

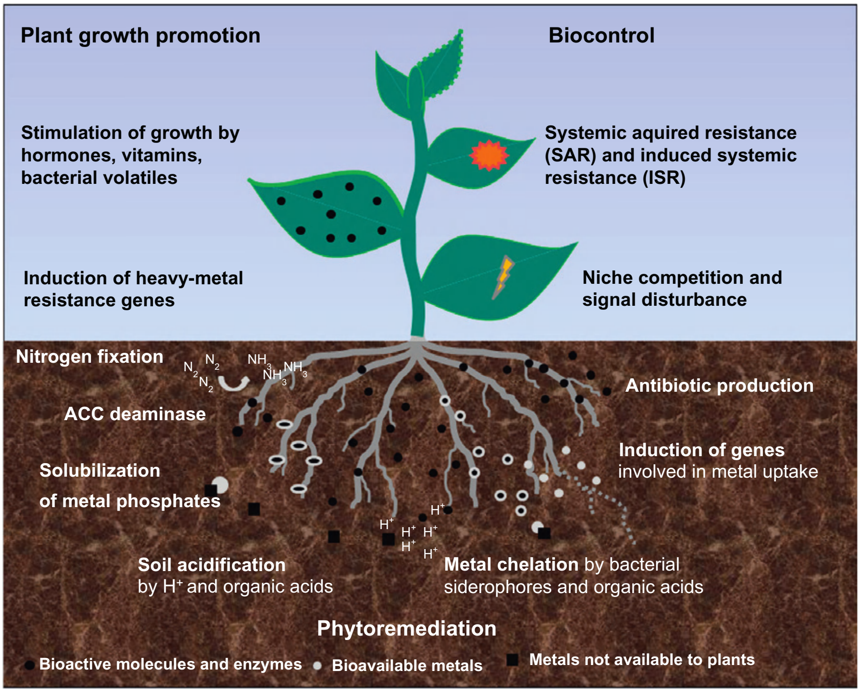

Figure 7.1 Potential beneficial effects of plant-associated bacteria on plant growth and health.

atmospheric nitrogen (N_2) is reduced to ammonia (NH_3) by the enzymatic activity of nitrogenases. Plants can assimilate NH_3 to produce nitrogenous biomolecules. In the context of plant–soil–microbe interactions, we distinguish between three main groups of nitrogen-fixing bacteria: (i) free-living, diazotrophic soil bacteria, such as *Azotobacter*; (ii) diazotrophic bacteria establishing associations with plants endophytically or epiphytically, such as *Azospirillum*; and (iii) bacteria forming tight symbiosis with plants by elicitating the formation and colonization of specialized organs, the root nodules, such as rhizobia.

Symbiotic nitrogen fixation has doubtless great impact on plant nutrition and is an integral component of sustainable agriculture (Sessitsch et al., 2002b). It has been estimated that symbiotic nitrogen fixation makes up at least 70 million metric tons of nitrogen per year worldwide (Brockwell and Bottomley, 1995). Despite the optimistic expectations on the impact of associative diazotrophic nitrogen fixation, most inoculation experiments did not show substantial contribution to plant growth (Dobbelaere et al., 2003).

Table 7.1 Observed effects of plant-beneficial bacteria in regard to plant growth promotion

Proposed mechanism PGPR/endophyte	Plant	Experimental conditions	Plant response to PGPR/endophyte inoculation	References
Phytohormone production—indole-3-acetic acid (IAA)				
Paenibacillus polymyxa RC05, *Bacillus* spp. RC23	Strawberry	Field trial	Increased yield, average fruit weight, and quality fruit ratio up to 21%, 19%, and 32%, respectively	Erturk et al. (2012)
Azospirillum brasilense strain SM	Sorghum	Axenic	Increased shoot length (29%) and dry biomass (83%) compared to control	Kochar and Srivastava (2012)
Pseudomonas aeruginosa Am3	Wheat	Axenic/pot trials	Increase in spike length (33%), number of tillers (71%), and weight of seeds (39%)	Hussain and Hasnain (2011)
Providencia sp. WRB4, *Alcaligenes* sp. WRB10	Wheat	Pot trial	Increased plant biomass (18%) and grain yield (94%)	Manjunath et al. (2011)
Enterobacter cloacae GS1	Rice	Axenic/pot trials	Significant increase in fresh plant weight, root length, shoot length, and N-content	Shankar et al. (2011)
Bacillus licheniformis MML2501	Groundnut	Axenic/pot trials	Increase in seed germination (90%), shoot length (44%), root length (55%), plant biomass, (67%) and grain yield (155%)	Prashanth and Mathivanan (2010)
Bacillus sp. NpR-1, MiR-4, *Pseudomonas* sp. AvH-4, *Staphylococcus* CdR-1, *Escherichia* sp. SnR-1	Wheat	Axenic/pot trial	Increase in shoot length, no. of tillers/plant, and spike length up to 29%, 97%, and 25%, respectively	Ali et al. (2009)
Azospirillum brasilense SM	Sorghum	Axenic	Improved shoot length and seedling dry weight up to 28% and 62%, respectively	Malhotra and Srivastava (2009)

Continued

Table 7.1 Observed effects of plant-beneficial bacteria in regard to plant growth promotion—cont'd

Proposed mechanism PGPR/endophyte	Plant	Experimental conditions	Plant response to PGPR/endophyte inoculation	References
Bacillus sp. SVPR30	Rice	Greenhouse	39% increase in plant dry biomass	Beneduzi et al. (2008)
Azospirillum brasilense Sp245 and an IAA-deficient mutant	Wheat	Greenhouse	Seeds inoculated with wild-type strain gave 12% and 25% higher plant biomass and ears number compared with the IAA-deficient mutant and uninoculated seeds	Spaepen et al. (2008)
P. putida subgroup B strain 1	Tomato	Greenhouse	15% increase in tomato fruit	Gravel et al. (2007)
Burkholderia sp. 1, *Pseudomonas* sp. 10	Kidney bean	Sterile water	Increased stem height up to 7.8-fold (*Pseudomonas*) and threefold higher root number (*Burkholderia*)	Tsavkelova et al. (2007)
Rhizobacterial strains Ha 21, Ha 22, Ha 23, Ha30	Wheat	Pot/field trials	Stimulatory effects on grain yields in pot (up to 14.7% increase) and field experiments (up to 27.5% increase)	Khalid et al. (2004)
Pseudomonas putida GR12-2 and an IAA-deficient mutant	Canola, mungbean	Growth pouch/ sterile vermiculite	Seeds inoculated with wild-type gave 35–50% longer roots compared to the IAA-deficient mutant and the roots from uninoculated seeds	Patten and Glick (2002)
Phytohormone production—indole-butyric acid (IBA)				
Azospirillum brasilense UAP 154	Maize	Axenic	Increased 74% higher root dry weight	Martinez-Morales et al. (2003)

Phytohormone production—gibberellins				
Burkholderia sp. KCTC 11096BP	Cucumber	Pot trial	Increased shoot length, shoot and root biomass, and chlorophyll contents up to 40%, 38%, 32%, and 10%, respectively	Kang et al. (2010)
Bacillus cereus MJ-1	Red pepper	Pot trial	Increased plant height, root length, and biomass up to 14%, 50%, and 30%, respectively	Joo et al. (2004)
Bacillus licheniformis CECT 5106 and *B. pumilus* CECT 5105	*Pinus pinea* L.	Pot trial	Increased root length (92%) and dry biomass (83%)	Probanza et al. (2002)
Phytohormone production—cytokinins				
Bacillus subtilis, strain IB-22	Wheat	Axenic	Increased seedling biomass, up to 16%	Arkhipova et al. (2006)
Pseudomonas BA-8, *Bacillus* OSU-142	Sweet cherry	Field trials	Increased fruit yield, up to 16%	Esitken et al. (2006)
ACC deaminase activity				
Serratia proteamaculans J119	*Cicer arietinum* L.	Axenic/pot/field trials	Increase in root weight, shoot weight, number of pods, and grain yield up to 51%, 52%, 92%, and 60%, respectively	Shahzad et al. (2010)
Pseudomonas entomophila strain PS-PJH	*Raphanus sativus*, *Lactuca sativa*	Axenic	Increased seedling vigor in *R. sativus* (43%) and *L. sativa* (34%) plants	Kamala-Kannan et al. (2010)

Continued

Table 7.1 Observed effects of plant-beneficial bacteria in regard to plant growth promotion—cont'd

Proposed mechanism PGPR/endophyte	Plant	Experimental conditions	Plant response to PGPR/endophyte inoculation	References
Pseudomonas putida UW4	*Arabidopsis thaliana*	Axenic	Increased root hair length (2.35-fold)	Contesto et al. (2008)
Rhizobium sp. strain TAL1145, transconjugants of TAL1145	*Leucaena leucocephala*	Leonard jar	Multiple copies of the native- and BL3-*acdS* genes in TAL1145 resulted in significant increases in numbers and dry weight of nodules compared to native strain TAL1145	Tittabutr et al. (2008)
Methylobacterium fujisawaense strains CBMB 20, CBMB 10	Canola	Gnotobiotic	Increased root length up to 78%	Madhaiyan et al. (2008)
Burkholderia caryophylli ACC7, *Pseudomonas fluorescens* ACC50	Wheat	Pot/field trials	Increase in root weight and grain yield up to 83% and 43% (*B. caryophylli*), *Pseudomonas* sp. performed better under field conditions	Shaharoona et al. (2007)
Pseudomonas putida biotype A, *P. fluorescens*, *P. fluorescens* biotype G	Maize	Pot trial	Improved plant biomass and cob weight up to 12% and 20%, respectively	Shaharoona et al. (2006)
Pseudomonas spp. strains PGPR1, PGPR2, PGPR4, PGPR7	*Arachis hypogaea* L.	Axenic/pot/field trials	Significantly enhanced pod yield (23–26%, 24–28%, and 18–24%, respectively), haulm yield, and nodule dry weight under field conditions	Dey et al. (2004)
Nutrient solubilization/uptake—P-solubilization				
Pontibacter niistensis NII-0905	Cowpea	Axenic	1.3-fold increase in seedling biomass	Dastager et al. (2011)

Pseudomonas fluorescens strain DR54 and *Enterobacter radicincitans* strain DSM 16656	Maize/oilseed rape	Pot/field trials	*P. fluorescens* is more effective in P mobilization than *E. radicincitans*	Krey et al. (2011)
Micrococcus sp. NII-0909	Cowpea	Pot trial	Higher root (100%) and shoot (39%) lengths and biomass (54%)	Dastager et al. (2010)
Pantoea sp. DHRSS, *Citrobacter* sp. PP1	Pigeon pea	Axenic/pot trials	Inoculation with *Pantoea* strain PP1 and *Citrobacter* strain DHRSS improved significantly shoot biomass and P-content compared to control	Patel et al. (2010)
Streptomyces filipinensis no. 15	Tomato	Gnotobiotic conditions	Increased root–shoot length (1.1- and 1.03-fold) and root–shoot weight (2.6- and 2.7-fold)	El-Tarabily (2008)
Nutrient solubilization/uptake—N_2-fixation/uptake				
Klebsiella sp. LGI4RJ	Canola	Greenhouse	Significant increase in shoot N-content	Farina et al. (2012)
Bacillus subtilis OSU-142, *Azospirillum brasilense* Sp245	Grapevine	Pot trial	Significantly improved the chlorophyll concentrations of the leaves (*A. brasilense*) and stimulated vegetative development and mineral acquisition of the plants (*B. subtilis*)	Sabir et al. (2012)
Bacillus amyloliquefaciens IN937a and *Bacillus pumilus* T4	Tomato	Greenhouse	Increased nitrogen uptake	Adesemoye et al. (2010)
Azospirillum brasilense strain Sp7, *Bacillus sphaericus* strain UPMB10	Banana	Hydroponics	Increased the bunch yield up to 51%	Mia et al. (2010)

Continued

Table 7.1 Observed effects of plant-beneficial bacteria in regard to plant growth promotion—cont'd

Proposed mechanism PGPR/endophyte	Plant	Experimental conditions	Plant response to PGPR/endophyte inoculation	References
Azospirillum amazonense	Rice	Greenhouse	Increased dry matter and N accumulation up to 18% and 27%, respectively	Rodrigues et al. (2008)
Pseudomonas sp. strain K1	Rice	Pot trial	Increased dry weight and yield up to 60% and 93%, respectively	Mirza et al. (2006)
Nutrient solubilization/uptake—siderophore production				
Ochrobactrum haematophilum H10	Cucumber	Pot trial	Leaf and root length were increased by 27% and 58%, respectively	Zhao et al. (2012b)
Streptomyces strains AzR-051	Tomato	Axenic	Increased root and shoot length up to 31% and 30%, respectively	Verma et al. (2011)
Bacillus subtilis CAS15	Pepper	Pot trial	36.92% and 49.68%, increase in fruit weight (37%) and yield (50%)	Yu et al. (2011)
Pseudomonas fluorescens R81	*Vigna mungo*/ *Triticum aestivum*	Pot/field trials	Improved grain yield up to 46%	Saharan et al. (2010)
Pseudomonas sp. strain GRP3	Mung bean	Pot trial	Increased shoot mass, root mass and total chlorophyll content up to 101%, 39%, and 40%, respectively	Sharma et al. (2003)

Moreover, nitrogen fixation by associative diazotrophs has been rarely proven, but these bacteria exhibit several other plant growth-promoting activities, such as the synthesis of plant hormones and vitamins, the improvement of nutrient uptake, induction of stress resistance, or stimulating nodulation of legumes by rhizobia (Dobbelaere et al., 2003).

4.1.2 Production of plant hormones, vitamins, and bacterial volatiles

Many plant-associated bacteria synthesize plant growth regulators such as hormones and volatiles. Phytohormones produced by bacteria are mainly cytokinins, auxins, and gibberellins. Interestingly, there seems to be plant organ-specific differences in the type of phytohormone produced by plant-associated bacteria. Whereas auxins were identified in isolates of any type of plant organ, gibberellins were typically found in root-associated bacteria and cytokinines in leaf-colonizing bacteria (Pirttilä, 2011).

Auxins are indole derivatives that play a central role in plant growth and are essential for plant body development. Genes involved in the production of indole-3-acetic acid (IAA), the major naturally occurring auxin, are frequently found in plant-associated bacteria, and it is believed that approximately 80% of rhizobacteria produce IAA (Khalid et al., 2004). There is evidence that IAA synthesis in bacteria might be stimulated by plant signals. The expression of IAA synthesis genes in *Azospirillum brasilense* is upregulated by IAA (van de Broek et al., 1999). The role of bacterial IAA synthesis in plant growth promotion is well documented (Lambrecht et al., 2000; Spaepen et al., 2007; Steenhoudt and Vanderleyden, 2000) and has been proven in the interaction between canola and *P. putida* GR12-2 (Patten and Glick, 2002). Canola roots inoculated with a mutant deficient in synthesis of IAA showed significantly reduced growth in comparison to roots colonized by the wild type (Patten and Glick, 2002). Besides the direct effects on plant growth and development, IAA indirectly affects plant nutrition by stimulating nitrogen fixation activity and P-solubilization (Bianco and Defez, 2010; Imperlini et al., 2009). A variant of *Sinorhizobium meliloti* 1021, strain RD64, with enhanced IAA synthesis ability showed improved nitrogen fixation ability as compared to the wild-type strain (Imperlini et al., 2009). Strain RD64 also showed enhanced P-solubilization activity reflected by the upregulation of genes coding for the high-affinity P transport system, the induction of acid phosphatase activity, and the increased secretion into the growth medium of malic, succinic, and fumaric acids (Bianco and Defez, 2010). On the other

hand, gene expression microarray analysis with *in vitro* plantlets of potato inoculated with the IAA-producing endophyte *B. phytofirmans* PsJN revealed no changes for genes responsive to auxin (Trognitz et al., 2008).

Although not as intensively studied as auxins, cytokinins and gibberellins have also been reported to stimulate plant growth (Cassán et al., 2009; van Loon, 2007). Cytokinins comprise a group of compounds with either an adenine or a urea backbone and regulate cytokinesis in plants (Skoog and Armstrong, 1970). In particular, they are involved in the induction of seed germination, the break of dormancy of buds, and apical dominance. Additionally, they induce chlorophyll synthesis and chloroplast proteins in the early leaf development (Skoog and Armstrong, 1970). Gibberellins stimulate plant growth in stems and leaves and modulate in certain species flowering time and the development of flowers, fruits, and seeds (Sun and Gubler, 2004). The importance of gibberellins can be seen with the gal-3-deficient *Arabidopsis* mutant, which is a nongerminating, extreme dwarf, late flowering, and male-sterile.

The role of cytokinin signaling in plant growth promotion by *Bacillus megaterium* has been studied with *Arabidopsis thaliana* mutants in which cytokinin receptors were disrupted (Ortíz-Castro et al., 2008). *B. megaterium* showed reduced plant growth promotion in mutants lacking one or two receptors, whereas a cytokinine receptor triple knockout of *Arabidopsis* did not respond at all to inoculation with *B. megaterium*.

Some PGPB are able to produce vitamins, especially B-group vitamins (Ivanova et al., 2006; Marek-Kozaczuk and Skorupska, 2001). Mutants of *P. fluorescens* strain 267 impaired in the synthesis of thiamine and niacin lost the ability to promote growth of red clover roots. The niacin auxotroph fully failed in colonizing red clover (Marek-Kozaczuk and Skorupska, 2001). Vitamins may also exhibit synergistic effects on other plant growth-promoting mechanisms. B-group vitamins produced by *Pseudomonas* sp. strain 267 stimulated symbiotic nitrogen fixation activity of *Rhizobium leguminosarum* bv. *trifolii* in clover (Derylo and Skorupska, 1993).

The emission of volatiles is a recently discovered novel mechanism by which bacteria promote plant growth (Ping and Boland, 2004; Ryu et al., 2003a). Ryu et al. (2003a) demonstrated that 2*R*,3*R*-butanediol and acetoin produced by *B. subtilis* GB03 and *B. amyloliquefaciens* IN937a significantly enhance growth in *Arabidopsis*. Tests with mutants of *A. thaliana* indicated that 2*R*,3*R*-butanediol and acetoin act via the modulation of cytokinin and ethylene signaling (Ryu et al., 2003a).

4.1.3 1-Aminocyclopropane-1-carboxylate deaminase

Ethylene affects growth and development in plants. It regulates cell size and cell division, and in terms of development, ethylene is involved in ripening, senescence, and abscission (Schaller, 2012). 1-Aminocyclopropane-1-carboxylate (ACC) is an immediate precursor in the synthesis of ethylene in plants and is degraded by ACC deaminase enzymes to 2-oxobutyrate and ammonia. This enzyme activity is frequently found in soil microorganisms (Glick et al., 2007). ACC deaminase may play a role in balancing the plant ethylene levels (Glick et al., 2007). Glick et al. (2007) suggested the following mechanism: ACC deaminase-producing rhizosphere bacteria degrade ACC directly when it is excreted by plant roots. As a consequence, the amount of ethylene is decreased and the plant protected from growth-retarding effects of high ethylene levels produced by plants in response to biotic and abiotic stress (Glick, 2005). This idea is supported by the finding that canola (*Brassica napus*) roots colonized by the ACC deaminase-producing *P. putida* UW4 upregulate genes involved in cell division and proliferation but downregulate stress-related genes (Hontzeas et al., 2004). More recently, it has been shown that during inoculation of *B. napus* with *P. putida* UW4 defective in ACC deaminase activity, plant genes for auxin responsive factors were upregulated and stress-responsive genes were downregulated (Stearns et al., 2012) as compared to the wild-type strain. However, the role of ACC deaminase enzyme activity in plant growth promotion has been clearly demonstrated in the symbiosis of *B. phytofirmans* PsJN and canola. Sun et al. (2009) constructed a knockout mutant of *B. phytofirmans* PsJN lacking ACC deaminase activity. The mutant was no longer able to promote the elongation of the roots of canola seedlings (Sun et al., 2009).

4.1.4 Iron uptake and phosphate solubilization

Many Gram-negative bacteria synthesize and excrete siderophores, molecules with high affinity to iron. The main groups of siderophores are the hydroxamates and catecholates (Miethke and Marahiel, 2007). The siderophores excreted into the extracellular environment bind iron. The resulting ferric–siderophore complexes are recognized then transported into the cell via specific receptor proteins (TonB-dependent receptors). The effect of microbial siderophores in promoting plant growth might be indirect. Kloepper et al. (1980) proposed that siderophores produced and released by PGPR deprive the native microflora of iron which led to the suppression of potential pathogenic bacteria. Furthermore, siderophores contribute to the rhizosphere competence of bacteria that synthesize plant hormones or exhibit ACC deaminase activity (Crowley, 2006). On the other hand, plants were found to

be able to take up microbial ferric–siderophores complexes (Crowley et al., 1988). However, the proof that the symbiosis between plants and siderophore-producing bacteria results in better iron supply of plants is still missing (Crowley, 2007). Phosphate is probably the most limiting factor in plant growth, and although P is abundant in soils, the bioavailable soluble form of phosphate is limited. Because of the negative charge of the phosphate ion, they quickly form insoluble mineral complexes which are not available for plants. In addition, high amount of phosphate is fixed in organic matter. Many PGPR have the potential to release fixed P, whereby different mechanisms are involved in inorganic or organic phosphate solubilization (reviewed by Rodriguez et al., 2006). In principle, inorganic phosphate-solubilizing bacteria produce and excrete small organic acids such as gluconic, citric, lactic, propionic, and/or succinic (Chen et al., 2006; Vyas and Gulati, 2009). The hydroxyl and carboxyl groups bind the cations in mineral phosphate complexes releasing soluble phosphate (Kpomblekou and Tabatabai, 1994). The release of phosphate from organic matter is maintained by the activity of three types of enzymes: nonspecific phosphatases, phytases, and phosphonatases or C–P lyases. The ecologically most relevant enzymes are the acid phosphatases and phytases because of the predominance of their substrates in soil. Phosphatases catalyze the dephosphorylation of phosphoesters or phosphoanhydride bonds in general, whereas phytases act specifically on phytic acid. Phosphonatase and C–P lyases catalyze the cleavage of C–P bonds in organophosphonates (Rodriguez et al., 2006).

The most efficient phosphate-solubilizing bacteria known so far include strains of the genera *Pseudomonas*, *Bacillus*, *Rhizobium*, *Micrococcus*, *Flavobacterium*, *Burkholderia*, *Achromobacter*, *Erwinia*, and *Agrobacterium* (Vyas and Gulati, 2009). Recently, Trivedi and Sa (2008) reported the correlation of inorganic phosphate solubilization efficiency and plant growth promotion intensity in *Pseudomonas corrugata* (NRRL B-30409). Two mutants of the strain with enhanced ability to solubilize rock phosphate exhibited also enhanced plant growth-promoting activity (Trivedi and Sa, 2008).

4.1.5 Photosynthesis and polyamines

Plant inoculation with many PGPR and endophytes results in increased chlorophyll content and photosynthesis activity. *Bacillus pumilus* and *Acinetobacter johnsonii*, respectively, significantly increased the maximum photochemical yield and total chlorophyll content in leaves of sugar beet (Shi et al., 2010). Bacterization of *Vitis vinifera* L. cv. Chardonnay (grapevine) by *Burkholderia phytofirmans* PsJN resulted in a 1.3 times higher

CO_2-fixation rate and a 2.2 times higher O_2 evolution as compared to non-inoculated control plants (Ait Barka et al., 2006). More recently, Fernandez et al. (2012) monitored various photosynthesis parameters such as net photosynthesis, intercellular CO_2 concentration, stomatal conductances, activity of photosystem II, and total chlorophyll concentration in cold-stressed grapevine plantlets inoculated with *B. phytofirmans* PsJN as compared to nonbacterized controls. The authors clearly showed that the increase in plant photosynthetic activity was not due to a modulation of stomata conductance in grapevine colonized by strain PsJN. Thus, the mechanism underlying the stimulation of plant photosynthesis by *B. phytofirmans* PsJN remains elusive. Recently, the genome of *B. phytofirmans* PsJN was fully sequenced (Weilharter et al., 2011). Based on the occurrence of pfam domains and sequences affiliated to certain COG categories, we identified eight genes for carbonic anhydrase (CA) in the genome of *B. phytofirmans* PsJN (unpublished data). The CAs represent a family of enzymes that catalyze the reversible conversion of carbon dioxide and water to bicarbonate and protons (Badger and Price, 1994). In plants, CAs help raising the concentration of CO_2 in order to increase the carboxylation rate of the enzyme ribulose-1,5-bisphosphate carboxylase oxygenase (Badger and Price, 1994). However, the activity and functionality of the putative CA genes in strain PsJN have not been analyzed and we may only speculate whether strain PsJN directly modulates CO_2 levels in the host plant.

Microbial photosynthetic activity or at least the presence of relevant genes has been shown for various plant-associated *Proteobacteria* such as *Bradyrhizobium* spp. (Giraud et al., 2007; Hungria et al., 1993), *S. meliloti* (Pickering and Oresnik, 2008), or *Azospirillum amazonense* (Sant'Anna et al., 2011). All photosynthetic strains encode one or more bacteriophytochromes (Jaubert et al., 2008; Kaneko et al., 2010; Sant'Anna et al., 2011) and gene cluster implicated in carbon fixation via the Calvin–Benson–Basham cycle including ribulose-1,5-bisphosphate carboxylase genes. All of these strains are nitrogen-fixing bacteria, and it is supposed that the central role of photosynthetic activity is during the initial steps of the symbiosis between bacteria and plants by ensuring survival of the bacteria and later on in the plant by generating the energy needed for nitrogen fixation (Giraud et al., 2007).

4.2. Biocontrol properties against plant pathogens

Many plant-associated bacteria have the ability to protect plants from pests. Some examples of rhizosphere and/or endophytic bacteria with biocontrol

properties against different pathogens are given in Table 7.2. Biocontrol of pathogen infections can be achieved directly or indirectly. The principal mechanisms involved in biocontrol by endophytic and soil bacteria are illustrated in Fig. 7.1 and have been summarized in a number of reviews (Berg, 2009; Francis et al., 2009; Schrey and Tarkka, 2008; Tarkka et al., 2009; Zamioudis and Pieterse, 2012). Bacteria may act directly

- by niche occupation, which means by colonizing the rhizosphere or phyllosphere and thereby occupying the physical niche for plant pathogens, by limiting nutrients required for pathogen growth, and by competing for limiting elementary nutrients such as iron;
- by producing signal components interfering with pathogen reproduction, toxin production, or virulence;
- by antibiosis, by producing toxins and antibiotics, by producing lytic enzymes, and by acting as parasites or predators of pathogens.

Indirect mechanisms of biocontrol include activation or alteration of plant defense or recruiting additional players in the plant–pathogen–beneficial bacteria interactions and might be achieved

- by inducing plant resistance,
- by stimulating plant hormones resulting in outgrowth or altered host acceptance,
- by attracting or stimulating additional organisms capable of inhibiting pest or pathogens.

Important factors for the execution of these mechanisms are molecular patterns associated with biocontrol strains (Pal and McSpadden Gardener, 2006). These can be all kind of secondary metabolites, for example, lipopeptides, phenazines, polyketides and pyrrolnitrin, surface and structural components of bacteria such as flagellins and lipopolysaccharides, metabolic (side) products such as ammonia or cyanide as well as proteins, and enzymes. Each biocontrol strain and even each involved chemical signal do not exclusively activate a single of the above described mechanisms but are regularly responsible for various direct and indirect biocontrol mechanisms. For example, *B. amyloliquefaciens* FZB42 produces different polyketides and the lipopeptides bacillomycin D, fengycin A, and surfactin (Chen et al., 2007), of which surfactin alone has been discussed to a play vital role in swarming, root niche colonization and occupation, in direct antibiosis toward bacteria and fungi, and in the activation of plant resistance (Ongena and Jacques, 2008). Even more ambivalent interactions have been described for the biocontrol activity of *Streptomyces* sp. GB 4-2 against *Heterobasidion* root and butt rot in Norway spruce seedlings (Lehr et al., 2008). While the bacterium even promotes

Table 7.2 Examples of rhizosphere and/or endophytic bacteria with biocontrol properties against different pathogens in various host plants

Biocontrol bacteria	Target pathogen/ diseases	Plants	References
Pseudomonas aeruginosa 7NSK2	*Botrytis cinerea*	*Phaseolus vulgaris*	de Meyer and Hofte (1997)
Pseudomonas fluorescens WCS374	*Fusarium* wilt	*Raphanus sativus*	Leeman et al. (1995)
S. marcescens 90-166, *Bacillus pumilus* SE34, *P. fluorescens* 89B61, *Bacillus pasteurii* C9, *Paenibacillus polymyxa* E681, *Bacillus subtilis* GB03, *Bacillus amyloliquefaciens* IN937a, *Enterobacter cloacae* JM-22, and *Bacillus pumilus* T4	*P. syringae* pv. tomato DC3000 and *P. syringae* pv. Maculicola ES4326	*Nicotiana tabacum*, *Capsicum annuum*, *Cucumis sativus*, *Solanum lycopersicum*, *Arabidopsis thaliana*	Wei et al. (1991, 1996), Raupach et al. (1996), Yan et al. (2002), Zhang et al. (2002), Ryu et al. (2003b)
Pseudomonas fluorescens WCS374	*Colletotrichum falcatum*/red rot disease	*Saccharum officinarum*	Viswanathan and Samiyappan (1999)
Pseudomonas putida 89B-27 and *Serratia marcescens* 90-166	*Fusarium oxysporum* f. sp. *cucumerinum*	*Cucumis sativus*	Liu et al. (1995)
Bacillus pumilus SE 34 p	*F. oxysporum* f. sp. *radicis-lycopersici*	*Solanum lycopersicum*	Benhamou et al. (1998)
P. fluorescens 63-28	*Pythium ultimum*	*Pisum sativum*.	Benhamou et al. (1996)
P. fluorescens 63-28	*F. oxysporum* f. sp. *radicis-lycopersici*	*Solanum lycopersicum*	M'Piga et al. (1997)
Bacillus cereus	*F. solani*, *Sclerotium rolfsii*	*Gossypium hirsutum*, *Phaseolus vulgaris*	Pleban et al. (1995)
P. fluorescens EP1	*Colletotrichum falcatum*	*Saccharum officinarum*	Viswanathan and Samiyappan (1999)

Continued

Table 7.2 Examples of rhizosphere and/or endophytic bacteria with biocontrol properties against different pathogens in various host plants—cont'd

Biocontrol bacteria	Target pathogen/ diseases	Plants	References
Serratia marcescens 90-166, *Bacillus pumilus*, and *Pseudomonas fluorescens* 89B-61	*P. tabacina*	*Nicotiana tabacum*	Zhang et al. (2002)
Pseudomonas aeruginosa 7NSK2 p	*Botrytis cinerea*	*Solanum lycopersicum*	Audenaert et al. (2002)

growth of the pathogen, it also induces local and systemic defenses in Norway spruce thereby increasing resistance to the rot pathogens.

4.2.2 Outcompetition of pathogens

Looking more closely at these involved mechanisms, niche occupation as competition for space, nutrients, and physical niches of the rhizosphere/rhizoplane and endophytic tissues (Fig. 7.1) can be exerted by different beneficial Gram-positive and Gram-negative bacteria. The root surface and surrounding rhizosphere are full of root exudates containing up to 40% of the photosynthates and are rich sources of nutrients including organic acids, sugars, vitamins, and amino acids. Thus, along root surfaces are suitable nutrient-rich niches that can attract a great diversity of microorganisms and also phytopathogens (Compant et al., 2005; Lynch, 1990). Competition for these nutrients and niches is a fundamental mechanism by which beneficial bacteria derived from the rhizosphere protect plants by depriving phytopathogens of essential nutrients. Chemotaxis toward nutrients exuded in the rhizosphere of the host plants could explain how niche occupation at the rhizosphere level is achieved (Compant et al., 2005). This implies that beneficial bacteria should have strong chemotactic abilities to reach exudate components before pathogens to be able to protect the plants (Compant et al., 2005).

A particularly limited nutrient is iron. Important factors in the competition for this nutrient are siderophores produced by certain bacteria as described firstly by Kloepper et al. (1980). Siderophores sequester iron (III) and are used largely by their producers and by certain plants (Datnoff et al., 2007). This limits the availability to other microbes and pathogens and suppresses their growth (Kloepper et al., 1980). Various bacteria are able

to produce siderophores, as, for example, members of *Actinobacteria*, *Gammaproteobacteria*, and *Alphaproteobacteria* (Bendale et al., 2010; Datnoff et al., 2007; Paulsen et al., 2005; Sayyed et al., 2005; Yamanaka et al., 2005). Beneficial bacteria from these phyla such as *Pseudomonas* spp., *Streptomyces* spp., and rhizobia secrete chemically different siderophores with high iron affinity, which can reduce the availability of iron for plant pathogens. The list of bacterial groups is not exhaustive, and many other beneficial rhizosphere and endophytic bacteria can secrete siderophores as well.

Dense biofilms can then be formed on nutrient-rich root surfaces by various beneficial bacteria such as *Pseudomonas* spp. or *A. brasilense*, which occupy root elongation zones and root hairs (Ramey et al., 2004). Such biofilms may be a physical barrier to root pathogens, but also endophytes can physically occupy specific niches. The causal agent of Pierce disease of grapevine, *X. fastidiosa*, is inhabitant of the xylem vessels (Hopkins, 2005). Certain strains of *X. fastidiosa* such as EB92-1 are nonvirulent and have been suggested as biocontrol agent of Pierce disease. A possible mechanism is the occupation of the xylem niches and competition, but other mechanisms such as induction of resistance have also been discussed for this strain (Hopkins, 2005).

4.2.3 Disturbance of pathogen signaling

Both Gram-positive and Gram-negative bacteria have been described to use cell-to-cell communication in a density-dependent manner to regulate, for example, biofilm formation, exopolysaccharide, and virulence factor production (Fuqua and Greenberg, 2002). These factors play important roles in the establishment of successful infections of phytopathogenic bacteria, and consequently, disturbance or interruption of this quorum signaling has the potential to inhibit plant diseases. One of the most prominent examples of quorum signaling is achieved by homoserine lactones of a number of Gram-negative bacteria including the phytopathogens such as *Agrobacterium* spp., *Dickeya* spp., and *Pectobacterium* spp. Degradation of homoserine lactones can be achieved by lactonases of *Bacillus* spp. or acylase of *Variovorax paradoxus* (Fuqua and Greenberg, 2002) and have been described for a number of other bacterial groups and strains, partly with other mechanisms such as oxidoreductases (Czajkowski and Jafra, 2009). Indeed, a homoserine-lactonase from a *B. amyloliquefaciens* strain (Yin et al., 2010) has been shown to inhibit carrot infection by *Pectobacterium carotovorum* ssp. *carotovorum* in laboratory tests and has the potential to act as biocontrol agent against *P. carotovorum*. However, this strategy might be problematic for field applications as it can also interfere with beneficial bacteria signaling, for example,

from rhizobia (Czajkowski and Jafra, 2009). Future applications of signal interference might be expanded to disturb signaling in fungi and *Oomycota*, as they also use chemical signaling, for example, in the communication of zoospores during plant infections (Cottier and Mühlschlegel, 2012; Kong et al., 2010).

4.2.4 Direct antagonism against phytopathogens

Beneficial microbes have also been described to produce a broad collection of secondary metabolites inhibiting the growth or acting as toxins against phytopathogens (Fig. 7.1). Similar or even identical metabolites might even be produced by different bacterial groups. For example, pyrrolnitrin is known from *Burkholderia* and *Pseudomonas* species (Raaijmakers et al., 2002). This antibiotic has shown activity against *Rhizoctonia solani*, *Botrytis cinerea*, *Verticillium dahliae*, and *Sclerotinia sclerotiorum* (Ligon et al., 2000). A wide variety of compounds with antibiotic activity have been identified in biocontrol strains including specifically produced lipopeptides and polyketides, but also more unregulated waste products of metabolism such as hydrogen cyanide (Pal and McSpadden Gardener, 2006). Described metabolites with antibiotic activity from biocontrol strains include compounds such as amphisin, cyclic lipopeptides, 2,4-diacetylphloroglucinol, hydrogen cyanide, oomycin A, phenazine, pyoluteorin, pyrrolnitrin, tensin, and tropolone produced by pseudomonads (Défago, 1993; de Souza et al., 2003; Nielsen and Sørensen, 2003; Raaijmakers et al., 2002) and lipopeptides, kanosamine, oligomycin A, xanthobactin, and zwittermicin A produced by *Bacillus*, *Streptomyces*, and *Stenotrophomonas* spp. (Hashidoko et al., 1999; Kim et al., 1999; Milner et al., 1996; Nakayama et al., 1999; Ongena and Jacques, 2008). Agrocin 84 can be also secreted by *Agrobacterium radiobacter* strains (Kerr, 1980), 2,3-de-epoxy-2,3-didehydro-rhizoxin by *Pseudomonas borealis* MA342 (Hokeberg et al., 1998). Also Enterobacteriaceae such as *Pantoea agglomerans* EH318 are known to produce metabolites with antibiotic activity such as pantocin A and B (Wright et al., 2001), but secondary metabolites secreted by beneficial bacteria are continuously explored and a large variety of metabolites having antibacterial as well as oomycetal and fungal activities very likely remain to be discovered, especially from the large reservoir of metabolite-rich actinobacteria (Qin et al., 2011). These are in fact an important source of antibiotics that are linked to the inhibition of phytopathogens. It has been shown that *Streptomyces* sp. S-70 and *Streptomyces* sp. TP-A0569 suppress infection of *Alternaria brassicicola* on Chinese cabbage seedlings (Igarashi et al., 2002) inhibiting the formation of infection hypha that is necessary for *A. brassicicola*

to accomplish its infection. Sasaki et al. (2001a) also identified new bioactive compounds TPU-0031-A and B produced by actinomycete *Streptomyces* sp. TP-A0556 against *Aspergillus fumigatus* TFO 886. They also found cedarmycins A from *Streptomyces* sp. TP A0456 and found it to be active against *Candida glabrata* IFO 0622, as well as *Cryptococcus neofonnans* ATCC90, *in vitro* (Sasaki et al., 2001b). Other compounds such as alnumycin were also reported in *Streptomyces* sp. DSM 11575 isolated from root nodules of *Alnus glutinosa* (Bieber et al., 1998) as well as actinomycin X2 and fungichromin from the endophytic actinomycete *Streptomyces galbus* strain R-5 showing antibacterial and antifungal activities *in vitro* against *Pestalotiopsis sydowiana*, a major pathogen of rhododendron (Shimizu et al., 2004). Additionally, *Streptomyces* sp. NRRL30562 produces antibiotics designated as munumbicins A-D40 possessing a wide-spectrum activity against phytopathogenic fungi like *R. solani* (Castillo et al., 2002). *Streptomyces* sp. NRRL30566, which was isolated from a fern-leaved grevillea (*Grevillea pteridifolia*), produced also novel wide-spectrum antibiotics named kakadumycins found to be effective against *Bacillus anthracis in vitro* (Castillo et al., 2003). The actinomycetes and the compounds mentioned above are a few examples of biocontrol actinomycetes and agroactive compounds isolated from actinomycetes.

It has been demonstrated also that beneficial bacteria from the rhizosphere and endophytes can secrete not only antibiotics but also lytic enzymes enabling to reduce the growth of various phytopathogens (Fig. 7.1). Enzymes like chitinases, cellulases, and 1,3-β-glucanases could be, for instance, secreted by beneficial bacteria. For example, biocontrol of *Phytophthora cinnamomi* was obtained by using a cellulose-producing isolate ATCC 39149 of *Micromonospora carbonacea*. Control of *Phytophthora fragariae* causing raspberry root rot was suppressed by 1,3-β-glucanases-producing actinomycete isolate (EF-72, EF-22, and EF-97; Valois et al., 1996). Chitinolytic enzymes produced by *B. cereus* strain 65 also appear to be responsible for biocontrol of *R. solani* (Pleban et al., 1997). Similarly, biocontrol of *Pythium ultimum* in the rhizosphere of sugar beet by *Stenotrophomonas maltophila* W5 is likely due to the production of extracellular proteases (Dunne et al., 1997). *Lysobacter enzymogenes* strains produce a number of extracellular enzymes including chitinases, glucanases, and proteases making them active against various fungi and oomycetes (Kobayashi et al., 2005). Strain *L. enzymogenes* C3 (formerly classified as *S. maltophila* C3) has been suggested as biocontrol agent against different fungi and *Pythium* spp. (Kobayashi et al., 2005), and its large reservoir of lytic enzymes makes *L. enzymogenes* act as a predatory strain causing lysis in plant pathogens.

While fungal hyperparasitic strains have been reported (e.g. *Ampelomyces quisqualis* attacking powdery mildews (Pal and McSpadden Gardener, 2006)), bacterial strains parasiting on phytopathogens have not been described yet. However, endophytic bacteria of soil fungi exist (Frey-Klett et al., 2007), leaving open the possibility that a similar bacterial biocontrol strain might be discovered in future. In this context, it is interesting to note that the type III secretion system of the biocontrol strain *P. fluorescens* KD is required for activity against the oomycete pathogen *P. ultimum* indicating that the systems target the oomycete, which is often indicative for parasitism on hosts (Rezzonico et al., 2005).

4.2.5 Indirect mechanisms of biocontrol: Induction of systemic resistance responses in plants

Beneficial bacteria from the soil environment and/or entering plant internal tissues may not only directly target the survival, reproduction, and virulence of phytopathogens but also protect indirectly, for example, throughout defense induction in plants to increase resistance to phytopathogenic infections. This induced resistance corresponds to a state of the plant, where previous contact with an induction agent, an allelochemical, a virus or an organism makes the plant not only locally but often systemically more resistant to later infections (Fig. 7.1; van Loon et al., 1998; Bakker et al., 2007). Systemic acquired resistance (SAR) is thereby referred to as resistance phenomenon occurring after infecting with necrotizing pathogen, while induced systemic resistance (ISR) occurs after plant contact with a number of beneficial bacteria and is especially well characterized for *P. fluorescens* (Bakker et al., 2007; Zamioudis and Pieterse, 2012). Both systemic resistances are effective against a broad spectrum of pathogens and even insect herbivores. Hereby, SAR is dependent on SA, while ISR phenomena require functional jasmonate and/or ethylene signaling (Bakker et al., 2007; Pieterse et al., 1998; Zamioudis and Pieterse, 2012). Interestingly, the independency on SA seems to be even the case for some beneficial bacterial strains belonging to *Pseudomonas* spp. and *Serratia marcescens*, which have the ability to produce SA themselves (Bakker et al., 2007). The effectiveness of SAR and ISR is, at least in *Arabidopsis*, dependent if SA or jasmonate/ethylene signaling is required for plant defense. However, recent research has been shown that modulating plant defense is not only dependent on these defense signaling hormones, but a complicated signaling network and almost all described plant hormones such as abscisic acid, auxin,

brassinosteroids, cytokinins, and gibberellins have been implicated to play a role in defense modulation and systemic resistance (Pieterse et al., 2009).

Beneficial microbes and specific substances (e.g., β-aminobutyric acid) do not result in a strong transcriptome change of treated plants as observed after pathogen challenge but are priming the plant defenses to result in a quick response when a pathogen infects systemic parts of the plants (Conrath et al., 2002; Jakab et al., 2001, 2005; Ton et al., 2005). For instance, challenge inoculation of plants with the leaf pathogen *Pseudomonas syringae* pv. tomato showed a faster and stronger defense induction when plants are ISR-positive, which means they have been treated with *P. fluorescens* strain WCS417r (Verhagen et al., 2004). In recent years, a considerable number of reviews on the mechanisms and applications of priming, plant immunity, and induced resistance have been published (see, e.g., Conrath, 2011; Gust et al., 2010; van Loon and Bakker, 2005; Zamioudis and Pieterse, 2012), and it seems that epigenetic mechanisms involved in the priming state (Conrath, 2011) could be even transferred vertically to next generations (Slaughter et al., 2012). For the actual execution of priming effects in plants, both a wide range of secreted or even volatile components and parts of structures on the surfaces of the microbes can be responsible of. These microbial-associated molecular patterns induce a systemic resistance toward different kinds of phytopathogens and include not only allelochemicals such as siderophores and antibiotics but also flagella, lipopolysaccharides, as well as many others (Bakker et al., 2007).

Apart from the effects of biocontrol bacterial strains on defense signaling, bacteria can also influence hormones involved in plant growth, which might result in faster growth and thereby escaping pathogen pressure both locally or timely. Importantly, all the mechanisms cannot be seen isolated, but of course, a strong interplay between plant hormonal pathways exist and effects on plant growth can have effects on plant defense and vice versa. The complexity of defense signaling networks and the role of classical growth hormones have been reviewed recently (Pieterse et al., 2009). Additional aspects of indirect biocontrol mechanisms include the wide range of potential tri- and multitrophic interactions. Such phenomena have been described for a number of parasitic wasps and mites, which are attracted by plant volatiles (e.g., by maize) released after pest feeding (Heil, 2008). Similarly, it has been recently suggested that infection of green pepper with whitefly might result in attracting plant-associated rhizobacteria, which in turn can elicit enhanced resistance to further pathogen attacks (Yi et al., 2011), and *Arabidopsis* roots have been shown to secrete L-malic acid after *P. syringae*

pv. tomato DC3000 attack, which attracts beneficial *B. subtilis* FB17 to colonize plant roots and to further protect plants against subsequent infections (Rudrappa et al., 2008). It remains to be seen how common such a recruitment of additional players is in beneficial plant–microbe interactions and if application of biocontrol strains also can attract additional beneficial bacteria.

4.3. Phytoremediation

Human activities such as mining, industry, traffic, agriculture, and military enhance the release of organic and inorganic pollutants in the environment. Consequently, soil, water, and air have been contaminated with different types of pollutants (Capuana, 2011; Mansour and Gad, 2010). Phytoremediation is an emerging green technology that uses living organisms mainly plants and their associated microbes to remediate toxic organics, metals, and radionuclides from soil, sediment, surface-, and groundwater (Bolan et al., 2011; Ma et al., 2011). It is an ecofriendly and cost-effective technology that is currently receiving considerable global attention (Glick, 2010).

Plants can remediate contaminated soil by different processes such as degradation, adsorption, absorption, accumulation, and volatilization of pollutants (Newman and Reynolds, 2005). Plants can have more than 100 million miles of roots per acre, which enhance the bioavailability of contaminants (Boyajian and Carreira, 1997). Plant root system improves soil structure which facilitates fast movement of water and gases through the soil. It also provides a biologically active soil region (i.e., rhizosphere), where enhanced microbial diversity, population, and metabolic activities improve plant growth, pollutant uptake, and degradation (Gerhardt et al., 2009; Newman and Reynolds, 2004; Wenzel, 2009). Inorganic contaminants cannot be degraded, but they can be remediated by plants via absorption followed by sequestration. For ideal phytoremediation, plants should have tolerance to high concentrations of pollutants, rapid growth rate, and produce high biomass and profuse root system (Garbisu et al., 2002).

A number of technologies can be included in the term of phytoremediation. For example, the process involves the degradation of organic pollutants by plant enzymes is known as phytodegradation (Wild et al., 2005). The transportation of contaminants into plant tissue and then their volatilization is called phytovolatilization (Terry et al., 1995). Another process in which plant absorbs the contaminants from the soil and water and deposits them in above-ground biomass is known as phytoextraction (Blaylock and Huang, 2000). In respect to phytoremediation of toxic

organic pollutants, which are slowly moved from soil to plant, rhizodegradation (i.e., degradation of organic pollutants by microbes in the rhizosphere) is the main mechanism of detoxification (McCutcheon and Schnoor, 2003). Plants can also stabilize contaminants in the soil, and this phytoremediation type is known as phytostabilization. Although different phytoremediation techniques were developed for the remediation of organic and inorganic pollutants (Pilon-Smits, 2005), rhizodegradation for organics and phytoextraction for inorganics were extensively studied and applied for the remediation of contaminated soil (Afzal et al., 2012; Bolan et al., 2011; Glick, 2010; Weyens et al., 2009a).

During rhizodegradation, interactions among root, root exudates, rhizosphere soil, and microbes play an important role in the degradation of organic pollutants. The rich microflora in the rhizosphere can mineralize organic contaminants using their own metabolic pathways before they can negatively impact the plant (Kuiper et al., 2004).

The effectiveness of phytoextraction of inorganics as an environmental-cleanup technology relies on many factors including the type of the plant, concentration of the contaminant, metal availability for plant uptake, and the plant's ability to absorb and accumulate metals in above-ground biomass (Aggarwal and Goyal, 2007; Ernst, 1996). Some plant species can tolerate and accumulate high amount of metals and were defined as hyperaccumulators (Baker and Brooks, 1989; Freitas et al., 2004). Effective remediation of metal-contaminated soil requires hyperaccumulators with characteristics of rapid growth and a high amount of biomass (Nie et al., 2002). However, the presence of high concentration of heavy metals slows the growth of the hyperaccumulators and inhibits biomass production (Mohanty et al., 1989; Sheoran et al., 1990). Similarly, one of the major limitations of rhizodegradation is that many plant species are sensitive to higher concentration of organic contaminants in soil (Chaudhry et al., 2005; Huang et al., 2005) and cannot effectively support the growth of soil microorganisms and contaminant degradation. To overcome this problem, interactions among pollutants, microbes, and plants have received great consideration because of the possible role of microbes on pollutant degradation and/or plant growth promotion in contaminated soil (Glick, 2010; Rajkumar et al., 2009; Weyens et al., 2009a).

4.3.1 Plant uptake of contaminants

During phytoremediation, different plant processes and mechanisms are involved in the tolerance, accumulation, complexation, volatilization, and degradation of contaminants (Cherian and Oliveira, 2005; Jabeen et al., 2009;

Pilon-Smits, 2005). The contaminants uptake in plants mainly occurs through the root system. Plant roots show variation in the uptake of organic and inorganic contaminants from soil. Organic contaminants are usually man-made or released in the environment due to human activities and xenobiotic to the plant. As a result, the plant membrane does not possess transporter proteins for these organic contaminants. Therefore, organic contaminants are taken up by the plants through simple diffusion and depend on the hydrophobicity of the contaminant (Alkio et al., 2005; Kuhn et al., 2004). Hence, the transportation of organic compounds into plants is a physical rather than biological process (Davis et al., 2003). As inorganics (nutrients) are required by the plants for their own growth and metabolic activities, inorganics move into plants by biological processes via membrane transporter proteins (Campbell et al., 2003; Geisler et al., 2005; Jabeen et al., 2009).

Generally, the detoxification of organic pollutants in plants involves transformation, conjugation, and sequestration (McCutcheon and Schnoor, 2003; Reichenauer and Germida, 2008). In transformation, the xenobiotics are made more polar and thus more water soluble by oxidation, reduction, or hydrolysis (Komives and Gullner, 2005). In conjugation, xenobiotics are made less toxic for the plant by making a complex with compounds such as sugars and peptides. Finally, modified xenobiotics are sequestered in the vacuole or covalently bonded to the molecules of the cell wall (Burken, 2003; Rea, 2007). In contrast to uptake and sequestration in plant tissues, many organic pollutants are completely mineralized in the rhizosphere of plants. Plant exudates induce microbial genes involved in the degradation of organic compound or act as a cometabolite to facilitate microbial pollutant degradation (Fletcher and Hegde, 1995; Leigh et al., 2002; Olson et al., 2003). Recently, we have observed that inoculated bacteria were metabolically active in the degradation of organic pollutants in the rhizosphere of different plants (Afzal et al., 2011; Andria et al., 2009; Yousaf et al., 2010b).

As inorganic pollutants are either nutrients themselves (e.g., nitrate, phosphate, copper, manganese, zinc) or chemically similar to nutrients (e.g., arsenate, selenate), therefore, plants naturally have transporter proteins for these pollutants (Abedin et al., 2002; Shibagaki et al., 2002). Inorganics also require transporter proteins for their movement from root endodermis to root xylem (Krämer et al., 1996; von Wirén et al., 1999). However, organics pass the membrane between root symplast and xylem apoplast by diffusion (Taiz and Zeiger, 2002). The movement of inorganic contaminants from leaf xylem to leaf cells involves another membrane transport step. Specific membrane transporter proteins uptake the inorganics and transfer

them into leaf cells, whereas organics reach the leaf symplast from the shoot xylem by simple diffusion. Once a pollutant reaches the leaf symplast, it may be localized in specific tissues or cellular sites. Generally, poisonous organic and inorganic contaminants are sequestered in sites where they can do the least disturbance to important cellular functions. In the cell, contaminants are generally localized in the vacuole or cell wall (Burken, 2003; Cobbett and Goldsbrough, 2002). At the tissue level, pollutants may be localized in the epidermis and trichomes (Hale et al., 2001; Küpper et al., 2004).

4.3.2 Microbial processes in phytoremediation

For a long period, PGPB have been largely applied in agriculture for facilitating plants to uptake nutrients from the environment or preventing plant disease. However, the combined use of plant- and pollutant-degrading bacteria, and/or PGPB is relatively a new concept in the field of bioremediation of contaminated soil and water (Glick, 2010; Weyens, et al., 2009a; Zhuang et al., 2007). Although some studies reported that fungi can enhance pollutant remediation potential of plants (Soleimani et al., 2010a,b), plant-associated bacteria (rhizo- and endophytic) are the most important group capable of improving phytoremediation potential of plants (Korade and Fulekar, 2009; Wang et al., 2011; Weyens, et al., 2009a,b; for an overview, see Table 7.3 and Fig. 7.1). These bacteria are ubiquitous in plant's environment and play an important role in plant growth and the phytoremediation of contaminants from soil and water.

Generally, plant-associated bacteria involved in phytoremediation possess pollutant-degrading and/or plant growth-promoting activities (Johnson et al., 2005; Koo and Cho, 2009; Zhuang et al., 2007). Although several different bacterial strains were reported, *Pseudomonas*, *Pantoea*, and *Methylobacterium* sp. strains were most frequently isolated from the rhizosphere and endosphere of different plants and reinoculated to host plant to enhance the remediation of organic and inorganic soil contaminants. A naphthalene-degrading strain, *P. putida* PCL1444, enhanced the phytoremediation of naphthalene from soil (Kuiper et al., 2002). In studies performed in our lab, *Pseudomonas* and *Pantoea* sp. strains, showing hydrocarbon-degrading (Tesar et al., 2002; Yousaf et al., 2010a), and *Pseudomonas* and *Methylobacterium* sp., strains showing heavy metal-resistant and plant growth-promoting activities (Idris et al., 2004, 2006; Kuffner et al., 2008), were isolated from the rhizosphere of different plants. Hydrocarbon-degrading strains could utilize all tested alkanes and contained *alkB* and CYP153 alkane hydroxylase gene. Heavy metal-resistant strains

Table 7.3 Successful application of rhizo- (RH) and endophytic (EN) bacteria to plants for the remediation of organic and inorganic contaminants from soil

Contaminant	Plant	Bacteria	RH/ EN	References
Petroleum oil	*Cyperus rotundus*	*Mycoplana*, *Pandoraea*, *Pseudomonas*, *Rhizobium*, *Rhodococcus*	RH	Jurelevicius et al. (2010)
Diesel	*Lolium multiflorum*	*Pantoea* sp. BTRH79, *Pseudomonas* sp. ITRH76, *Rhodococcus* sp. ITRH43	RH	Yousaf et al. (2010b), Afzal et al. (2011, 2012)
Naphthalene	*Lolium multiflorum*	*Pseudomonas putida* PCL1444	RH	Kuiper et al. (2001, 2004)
Chlorpyrifos	*Lolium multiflorum*	*Pseudomonas nitroreducens* PS-2	RH	Korade and Fulekar (2009)
Phenanthrene	*Hordeum sativum* L.	*Pseudomonas* sp. strains	RH	Anokhina et al. (2004)
Cadmium, zinc	*Salix caprea*	10 different rhizosphere bacteria	RH	Kuffner et al. (2008, 2010)
Chromium	*Brassica juncea*	*Pseudomonas* sp. PsA, *Bacillus* sp. Ba32	RH	Rajkumar et al. (2006)
Cadmium	*Vigna mungo*	*Pseudomonas aeruginosa* MKRh3	RH	Ganesan (2008)
Diesel	*Lolium multiflorum*	*Pantoea* sp. ITSI10, *Pseudomonas* sp. strains, *Rhodococcus* sp. ITRI43, *Enterobacter ludwigii* strains	EN	Yousaf et al. (2010b, 2011), Afzal et al. (2011, 2012)
2,4-Dichlorophenoxy acetic acid	*Pisum sativum*	*Pseudomonas putida* strain POPHV6	EN	Germaine et al. (2006)
Naphthalene	*Pisum sativum*	*Pseudomonas putida* VM1441 (pNAH7)	EN	Germaine et al. (2009)
Ni	*Thlaspi goesingense*	*Methylobacterium* sp. strain V3, *Sphingomonas* sp. strain pfB27, *Curtobacterium* sp. strain VKM, *Curtobacterium* sp. strain VKM	EN	Idris et al. (2004, 2006)

Table 7.3 Successful application of rhizo- (RH) and endophytic (EN) bacteria to plants for the remediation of organic and inorganic contaminants from soil—cont'd

Contaminant	Plant	Bacteria	RH/ EN	References
Ni	*Alyssum bertolonii*	*Microbacterium* O1, *Pseudomonas* B7, *Curtobacterium* C2, *Staphylococcus* A3, *Bacillus* B3, *Arthrobacter* F3B	EN	Barzanti et al. (2007)
Pb	*Brassica napus*	*Pseudomonas fluorescens* G10, *Microbacterium* sp. G16	EN	Sheng et al. (2008)
Zn and Cd	*Thlaspi caerulescens*	*Sphingomonas* sp., *Methylobacterium* sp.	EN	Lodewyckx et al. (2002)
Cd	*Lycopersicon esculentum*	*Methylobacterium oryzae* strain CBMB20 and *Burkholderia* sp.	EN	Madhaiyan et al. (2007)
Ni, Cu, Zn	*Ricinus communis*	*Pseudomonas* sp. M6, *Pseudomonas jessenii* M15	EN	Rajkumar and Freitas (2008)
Ni, Cr	*Brassica juncea*	*Enterobacter aerogenes*, *Rahnella aquatilis*	EN	Kumar et al. (2009)
Zn	*Orychophragmus violaceus*	*Flavobacterium* sp.	EN	He et al. (2010)

showed Zn, Cd, and Pb resistance and the ability to produce IAA, ACC deaminase, and siderophores. Recently, we observed that the inoculation of Italian ryegrass with rhizosphere bacteria, *Pseudomonas* sp. ITRH76 and BTRH79, showing hydrocarbon degradation and ACC deaminase activities, enhanced plant biomass production and hydrocarbon remediation from soil (Afzal et al., 2011, 2012; Yousaf et al., 2010b). van Aken et al. (2004a) isolated a hydrocarbon-degrading *Methylobacterium* strain from the rhizosphere of poplar trees. This strain improved plant growth and remediation of different hydrocarbons (van Aken et al., 2004b). Similarly, hydrocarbon-degrading *Pseudomonas* sp. strains were isolated from the rhizosphere of *Cyperus rotundus* L. (Jurelevicius et al., 2010).

Several PGPR have also been found to enhance phytoremediation of heavy metals from contaminated environment (Dimpka et al., 2008a,b;

Kuffner et al., 2008, 2010). These bacteria improve phytoremediation potential of plants by different mechanisms and, most certainly, depend on the production of plant growth-promoting hormones such as auxins, cytokinins, gibberellins, and ethylene (Forchetti et al., 2007; Perrig et al., 2007). These hormones can affect plant growth and development and consequently phytoremediation of inorganic pollutants (Aslantaş et al., 2007; Dimpka et al., 2009; Ryu et al., 2005).

Although endophytic bacteria exist in plant variably and transiently (van Overbeek and van Elsas, 2008), several recent studies have shown that they can enhance pollutant remediation potential of plants (Luo et al., 2011; Rajkumar et al., 2009; Weyens et al., 2009b; Yousaf et al., 2011). The potential of endophytes to show resistance to heavy metals and degrade organic pollutants probably originates from their exposure to various compounds in the plant/soil niche. Siciliano et al. (2001) observed that plants vegetated in xenobiotic-contaminated soil naturally recruited endophytes with the necessary pollutant-degrading genes. A methylotrophic endophytic bacterium that was isolated from poplar trees showed degradation capabilities of many organic pollutants, suggesting that the endophytic bacteria can be applied for the remediation of soil contaminated with organic pollutants (Van Aken et al., 2004a,b). Barac et al. (2004) reported that an endophytic bacterium, *P. putida*, enhanced yellow lupine plant tolerance to toluene and reduced the volatilization of toluene from the plant into the atmosphere. In another study, a *Pseudomonas* endophyte, capable to degrade herbicide, inoculated to pea plants reduced the accumulation of the herbicide into plant tissues (Germaine et al., 2006). Recently, Dashti et al. (2009) isolated *Pseudomonas* sp. diazotrophic endophytic bacterial strains showing more efficient hydrocarbon degradation. They suggested that these bacteria can be applied to enhance phytoremediation of hydrocarbon-contaminated soil without applying any nitrogen fertilizers, which makes the phytoremediation process more economical and environment friendly.

Endophytic bacteria isolated from different plants vegetated in contaminated soils exhibited different bacterial populations (Lodewyckx et al., 2002). In recent studies performed in our lab (Yousaf et al., 2010a,b), cultivation-dependent and -independent analysis showed that birdsfoot trefoil and Italian ryegrass vegetated in diesel-contaminated soil hosted distinct alkane-degrading bacterial populations. Specific genes encoding beneficial bacterial traits, such as the *ncc* responsible for Ni resistant and *alkB* and CYP153 genes responsible for alkane degradation, were determined to assess metal resistant and alkane degradation potential of endophytic

bacteria (Idris et al., 2004; Yousaf et al., 2010a). Furthermore, in a very recent metagenomic study of our lab revealed that a high population of endophytic bacteria, isolated from rice roots grown in an uncontaminated site, showing potential to degrade alkanes as well as aromatic hydrocarbons (Sessitsch et al., 2012). In another very recent study, heavy metal-resistant endophytic *Methylobacterium* strains were isolated from mangrove growing in a hydrocarbon-contaminated and uncontaminated soil (Dourado et al., 2012). Similarly, heavy metal-resistant endophytic bacteria were isolated from Cd-hyperaccumulator *Solanum nigrum* L. (Luo et al., 2011). These above-mentioned studies suggested that endophytic bacteria are the most promising resource and may be excellent candidates of bioinoculants for improving the phytoremediation efficiency. Upon exposure to inorganic contaminants such as heavy metals, plant-associated microbes can modify plant cell metabolism, so that plants are able to tolerate high metal concentrations (Welbaum et al., 2004).

5. APPLICATION POTENTIAL IN AGRICULTURE AND CONCLUDING REMARKS

As outlined above, numerous reports exist on the huge diversity of plant-associated bacteria and their various activities, which contribute to plant growth and health. Conventional agricultural practices have so far paid only little attention to beneficial plant–microbe interactions. Plant breeding generally focuses on the improvement of higher yields or development of stress- or disease-resistant plant lines but does not consider aspects supporting beneficial microorganisms. It is well known that different plant genotypes interact differently with microorganisms (Remans et al., 2007); however, this aspect has not yet resulted in breeding programs making use of a plant's capacity to interact more efficiently with microorganisms. One of the bottlenecks is the limited availability of high-throughput screening programs to select for efficient plant–microbe interactions. Remans et al. (2007) explored responsiveness to auxin for mapping of quantitative trait loci (QTL) in common bean, which could be also used as a screening method of QTLs being responsive to certain plant-beneficial bacteria. This might be particularly applicable for bacteria, which produce auxins and thereby cause plant growth-promoting effects. A better understanding of the mechanisms involved in and signals responsible for the interactions between plants and microorganisms might lead to the development of screening tools, which can be implemented in plant-breeding

programs resulting in plant lines making better use of naturally occurring plant growth-promoting microorganisms.

Alternatively, soil microbial communities may be managed to better support plant growth. Such a management might involve the application of certain agricultural practices to stimulate the soil microflora. Crop rotation, particularly with legumes, or the use of organic fertilizers is known to increase microbial diversity. Smart agricultural systems may, for example, make use of specific crop rotations stimulating specific types of bacteria frequently involved in plant growth promotion. As an example, for a long time, farmers mixed soil after legume cropping with soil in which nonlegumes were grown and thereby increased yields (Bashan, 1998). However, the most straightforward way to make use of microbial activities is the application of the microorganisms or their products directly in agriculture. Actually, inoculation of leguminous plants with rhizobia forming nodules and providing a great contribution to the nitrogen demand of the plant is a common practice. Already at the end of the nineteenth century, farmers "inoculated" legume seeds with soil containing rhizobia (Smith, 1992). Later on, the practice of legume inoculation developed to a common practice, and partly, for example, in Brazil, legumes such as soybean are not fertilized with nitrogen and only inoculated with selected rhizobial strains (Bashan, 1998).

Other plant-beneficial bacteria have been applied only rarely, although large-scale production in Russia in the 1930s and 1940s was reported (Bashan, 1998). However, inconsistent results were reported (see Bashan, 1998), and probably also due to the increasing availability of inorganic fertilizers, microbial inoculation was no longer used. Due to the limited availability of natural resources such as phosphorus and the increasing awareness to environmental problems, the application of microbial inoculants as biofertilizers, biostimulants, or biopesticides has attracted attention. Particularly, bacteria belonging to *Azotobacter* and *Azospirillum* have been applied to enhance nonlegume growth, and mainly *Bacillus* and *Pseudomonas* have been applied for biocontrol of plant diseases (Bashan, 1998; Bravo et al., 2011). Although advancements have been made to better understand the mechanisms underlying beneficial plant–microbe interactions and plant experiments performed under controlled conditions, for example, in the greenhouse, have shown great and highly promising effects, effects of field application remain inconsistent. This inconsistency may depend on various issues. One reason might be inappropriate strain selection. Beneficial bacteria are frequently selected based on their beneficial activities such as production of antimicrobial substances or hormones in the laboratory; however, it

is generally not known or investigated whether these effects are also expressed in the field. Secondary metabolite production or other processes are well known to be induced only under specific conditions or might be quorum sensing-dependent. This aspect needs to be considered when applying strains, which show activities, which are tightly controlled by environmental parameters. Furthermore, some PGPB have a broad host range colonizing different plant species; however, others target more specifically certain plant genotypes or may even interact well with some plant cultivars but not with others. Successful competition in the soil/plant environment is an additional aspect, which has to be considered. Soils are colonized by thousands of bacterial species, and therefore, any introduced microorganism has to be adapted to its new environment and compete with the resident microflora. Successful plant colonization is a prerequisite for conferring any plant-beneficial effects, but this aspect is generally not considered in microbial screening programs. Resistance to harsh environmental conditions such as drought, high temperature, salinity, or acidity may influence the competitive ability of an inoculant strain in such an environment.

Different inoculation methods have been developed. For a long time, peat-based inoculants, particularly for *Rhizobium*, have been applied; however, the quality has not been satisfactory also contributing to inconsistent effects in the field. Other approaches are liquid inoculation or seed coating. Generally, a formulation is required or recommended to help the microorganisms to perform better at the site of application (Xavier et al., 2004). Usually, a carrier material (such as peat) together with additives, which improve the stability of the formulation, protects the microorganisms from environmental influence during storage and transport. In addition, certain formulation components may support the coating of seed with microbial cells. Although several products exist on the market, improvement is still needed to warrant high microbial numbers and activity in the field (John et al., 2011). A promising approach, which has been addressed in the recent years, is bioencapsulation or microencapsulation of microbial cells leading to increased shelf-life and microbial activity (John et al., 2011).

Making better use of beneficial plant–microbe interactions has great potential to contribute to more sustainable agricultural practices and is in line with current policy priorities with regard to the protection of natural resources and food safety and security. However, we, on the one hand, need to better understand the mechanisms of interaction and communication or signaling between plants and microbes but also have to improve application and field technology. Finally, a more systemic approach investigating the

system involving soil, plant, microbes, and environment will be better able to solve problems related to application in agriculture rather than looking at individual components only.

ACKNOWLEDGMENT

This work was partly supported by a grant provided by the Austrian Science Fund (FWF): P21261, P22867, and P24201.

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CHAPTER EIGHT

The Buffer Power Concept and Its Relevance in African and Asian Soils

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Contents

Advances in Agronomy, Volume 121
ISSN 0065-2113
http://dx.doi.org/10.1016/B978-0-12-407685-3.00008-6

Abstract

"The Nutrient Buffer Power Concept," a revolutionary soil testing procedure developed and tested over more than three decades after laboratory and field experimentation in European, African, and Asian soils, looks at soil testing to devise appropriate and accurate fertilizer recommendations for many field crops such as rye, wheat, and maize among cereals, red gram among pulses, white clover among fodder crops, and black pepper and cardamom among perennial spice crops, with a totally new perspective, as compared to routine "text book" methods of soil testing. The center piece of the concept is the accurate quantification of a soil nutrient's buffer power, which is then integrated into routine soil test data to derive appropriate and accurate fertilizer recommendations. Results showed that plant uptake of phosphorus, potassium, and zinc, the principal test elements, were closely related to their buffer power, with a coefficient of determination of as much as 98%, rather than their routine soil test data. The author makes out a strong case to propagate the new idea on a global basis. The concept has received global scientific attention and was recently short listed (the only one from Asia) for the very prestigious U.S. $1 million Rolex Awards for Enterprise of the Rolex Foundation, Geneva, from among more than 3500 nominations.

1. INTRODUCTION

Many years ago, in one of the early editions of *Advances in Agronomy*, Roy W. Simonson writing a chapter entitled "Concept of Soil," noted: "Someone has said that the fabric of human life is woven on earthen looms—it everywhere smells of the clay." More than three decades later, we agronomists and soil scientists have come very far in our understanding of "the fabric of human life" which "everywhere smells of the clay." That "the fabric of human life" which is so very intimately linked to soil has dramatically changed is beyond dispute. Yet, there is no denying the fact that this "fabric of human life" will always be linked to the soil which is "the pragmatic, the reality, the entity that dictates much of what societies can do" (Boul, 1994). Soil, in my opinion, is that invaluable gift of God to life on planet Earth and can aptly be termed "The Soul of Infinite Life." Though the basic concept of soil, since its early description as a "thin mantle over the land surface" has vastly changed over the years, this thin mantle has always been the focal point since it is the medium for plant growth. For early man it was nothing more than a physical support for his predation. Quite likely, some areas were known to provide better footing than others, and some

were to be avoided if possible. It is amazing that even after decades of research in soil science, which has provided such invaluable information on this "thin mantle over the land surface" so crucial to the existence of life, human, plant, and animal, on planet earth, this basic instinct of predation has remained unchanged. How else can we explain the disdain and callousness so often witnessed in modern societies, propelled by an insatiable greed to acquire unlimited wealth, which leads to the abuse of soil, this invaluable gift of God to man? Undoubtedly, the earliest shift in attitude toward soils must have originated at a time when man began to grow food, rather than gather it as his ancestors did. In many ways, this shift in attitude was the precursor to modern-day soil science. Though this shift must have occurred in pre-Christian times, about 9000 years ago, and focused on the inevitability of a proportionally smaller land surface supporting a larger human population, it is only in recent times that we have witnessed the magnitude of the impact of this shift in attitude on human existence. Much land has become degraded and unsuitable for agriculture since a century ago. The 1992–1993 World Resources report (Stammer, 1992) from the United Nations on the status of the world soils contains very alarming conclusions. For example, nearly 10 million ha of the best farm lands of the world have been so ruined by human activity since World War II that it is impossible to reclaim them. Over 1.2 billion ha have been seriously damaged and can be restored only at a great cost. This loss in soil capability could mean that there will be enormous food shortages in the next 20–30 years and, as is but natural, the people of disadvantaged nations will suffer the most. Many factors have contributed to this alarming state of affairs, one of the prime factors being "high-input agriculture," or more specifically chemical agriculture, euphemistically known as the "green revolution," where unbridled use of chemical fertilizers led to soil ruination. Punjab, the "cradle of green revolution" in India is a testimony to this sad state of affairs, where unbridled use of chemical fertilizers to boost the yield of dwarf wheat and rice varieties has led to soil degradation, loaded the ground water with high amounts of fertilizer residues (especially nitrates from urea) that it is no longer potable, led to soil salinity, dried aquifers, and vanishing biodiversity due to continuous monoculture of wheat and rice. There are hundreds of acres of land stretches that have become barren, where once stood lush wheat and rice fields. Crop yields have plateaued or drastically declined. Two-thirds of the seriously eroded land is in Asia and Africa. About 25% of the cropped land in Central America is moderately to severely damaged. In North America, this is a small percentage—only 4.4%. Since the time of this "green revolution," food production has declined dramatically in 80 developing countries in the past decade. Soil degradation is the major factor. Nearly

40% of the world's farming is done on very small parcels of 1 ha or less (Robison et al., 1981). Ignorance and poverty characterize this situation. Yet, emphasis on agriculture has been confined mostly to large-scale farming. Large-scale farming, grand projects at huge costs and huge profits, have been the order of the day for many decades. In a lighter vein, it can be said that even the "lebens raum" concept of Adolf Hitler had an echo in the inevitability of this modern-day fact. What else can justify the ruthless conquest of vast territories of land by this master strategist who set out to conquer the world—or, more appropriately, the world's soils?

Despite the complexity of soil science and the emergent soil management practices, the basic concept of soil as a medium of plant growth can be expected to persist for an indefinite length of time. But it is becoming increasingly clear that the earlier views on soil as merely the "supportive medium" for plant growth is giving place to newer ones on "managerial concepts" of this supportive medium. This is amply illustrated by the shift in focus from the green revolution phase of the 1960s to mid-1970s where application of increasing quantities of soil inputs such as fertilizers and pesticides was emphasized, to the "sustainable agriculture" phase from the early 1980s to the present (probably to continue?). Sustainable agriculture places more reliance on biological processes by adopting genotypes to adverse soil conditions, enhancing soil biological activity and optimizing nutrient cycling to minimize external inputs, such as fertilizers, and maximize their efficiency of use. In fact, the paradigm of the earlier phase has given way to the emergent new paradigm (Sanchez, 1994) and this is clearly reflected in the dialogue of the world leaders during the Earth Summit in 1991 in Rio de Janeiro, Brazil, where Agenda 21 has incorporated six chapters on soil management issues (Keating, 1993). The focus of this review will be on the second paradigm inasmuch as prescriptive soil management is concerned with regard to understanding soil nutrient availability and its efficient management in crop production.

2. EFFICIENT PLANT NUTRIENT MANAGEMENT—THE KEY FACTOR IN SUSTAINABLE SOIL MANAGEMENT

Agricultural systems differ from natural systems in one fundamental aspect: while there is a net outflow of nutrients by crop harvests from soils in the first, there is no such thing in the second (Sanchez, 1994). This is because nutrient losses due to physical effects of soil and water erosion are continually replenished by weathering of primary minerals or atmospheric deposition. Hence, the crucial element of sustainability of crop production is the nutrient factor. But, of all the factors, the nutrient factor is the least resilient (Fresco and

Kroonenberg, 1992). The thrust of high-input technology, the hallmark of the "green revolution," in retrospect, or the moderation by low input technology, the foundation stone of sustainable agriculture, in prospect, both dwell on this least-resilient nutrient factor. If the pool of nutrients in the soil, both native and added, could be considered as the "capital," efficient nutrient management might be analogous to raising the "interest" accrued from this capital in such a way that there is no great danger of the erosion of this capital. Hence, sound prescriptive soil management should aim at understanding the actual link between the "capital" and the "interest" so that meaningful management practices can be prescribed.

2.1. Soil tests and nutrient "availability"

It is universal knowledge that soil tests are the basis for predicting nutrient "availability." There are, perhaps, as many soil tests for each nutrient as there are nutrients. This review will not dwell on the merits or demerits of any single soil test or group of them. Suffice it to say that fertilizer recommendations traditionally are made at the point where marginal revenues equal marginal costs, which involve some positive synergism (DeWit, 1992). The most common result of this approach is the vast build-up in the soil nutrient pool in intensively cultivated soils (Whitmore and van Noordwijk, 1994). Data in Table 8.1 indicate positive balances (in kg/ha/year) for N(61), P(23), and K(37) in intensive crop production systems (Frissel, 1978).

Table 8.1 Nutrient balance (kg/ha/year) in intensively managed arable soils

	N	P	K
Inputs			
Fertilizers	156	39	119
Other	32	–	9
Total	188	39	128
Outputs			
Harvest	103	16	91
Removal	24	–	–
Other			
Total	127	16	91
	Balance: 61	23	37

After Frissel (1978).

Over several decades, such positive balances can lead to a huge build-up of the nutrient capital, especially in the case of high-input, intensive agricultural systems as in the case of many European, North American, and Scandinavian countries. A dangerous consequence of such huge soil build-up is nutrient contamination of groundwater to such extremes that "environmental soil tests" become necessary to assess critical limits of nutrient pollution (Sharpley et al., 1993). Nitrogen is a prime candidate for this scenario, especially in the temperate zone. At the other end of the spectrum are the marginal areas of the tropical zone where inadequate replenishment of nutrient removal by crop growth and also nutrient loss by soil and water erosion has left that capital "in the red." Initially fertile Alfisols of much of Africa with subsequent severe depletion of N and P (Yates and Kiss, 1992) are an example of this nutrient "bankruptcy." Either way, contemporary soil tests are the basis on which prescriptive management practices are formulated.

2.2. Rating soil tests to define nutrient availability and a fertility index

Most soil test laboratories around the world use some kind of "rating system" to evaluate soil test values. These rating systems invariably use qualitative terms such as "low," "medium," or "high" to describe the availability of a specific plant nutrient. Admittedly, these terms denote different meanings in the context of availability of a particular plant nutrient and, at best, are empirical terminologies. This problem has been recognized by researchers over the years. Morgan (1935) suggested a scale of 1–10 with 8 equal to the point of no response. Bray and Kurtz (1945) used relative yield or percentage sufficiency to describe the degree of deficiency, with 100 defined as the point of no response. The index below 100 follows the curvilinear relationship between soil test values and yield without the addition of the element. Above 100, the index displays a straight-line relationship indicating the relative margin of adequacy or the proximity to an excessive level. To eliminate the need for a percent sign, the values are referred to as "Fertility Indices" and they are reported to the nearest multiple of 10 from 0 to 9990 (Cope and Evans, 1985). In addition to ratings, most laboratories use some method of reporting results more precisely, mainly for use by farmers in record keeping and monitoring soil fertility. Some report kg/ha, lb/a, or ppm extracted, but these would be confusing to farmers, because each element has a different level for a specific degree of adequacy (Cope and Evans, 1985). For instance, the adequate or critical level for one soil may be 25 ppm P, 120 ppm K, 200 ppm Ca, and 30 ppm Mg. Adequate

levels in other soils and from other extracting procedures would be different for each element (Cope and Evans, 1985).

Despite the fact that a number of soil tests and others such as Diagnosis and Recommendation Integrated Systems are in vogue to predict nutrient availability, it must be said that a universal picture is yet to emerge in this field with regard to precise availability prediction. This is primarily because a soil test in the laboratory can never simulate plant root absorption of a nutrient in a field soil, though most of the time the assumption is that it does. In the final analysis, it is the plant and plant alone which will decide whether or not the nutrient is available. This review examines the question of whether a better and more reliable alternative exists.

3. THE BUFFER POWER AND EFFECT ON NUTRIENT AVAILABILITY

3.1. Basic concepts

In any nutrient management approach that is sound and reproducible, one must start with a basic understanding of the chemical environment of plant roots. When we consider this, the first term that we come across is the “soil solution,” because the plant root is bathed in it and is most affected by its chemical properties. The Soil Science Society of America (1965) defines soil solution as “the aqueous liquid phase of the soil and its solutes consisting of ions dissociated from the surfaces of the soil particles and of other soluble materials.” Adams (1974) has given a simple definition: “The soil solution is the aqueous component of a soil at field-moisture contents.” Perhaps it is important to emphasize here that much of contemporary soil testing has considered a soil extract as synonymous with the soil solution. Since soil extraction is supposed to simulate plant root extraction, it is pertinent to consider the chemical environment of the root, though briefly, from this angle. It is worth noting that the chemical environment of roots in natural soil systems is so obviously complex that both soil scientists and plant physiologists have been unable to provide a precise definition. If this complex chemical system is to be accurately quantified, thermodynamic principles will need to be used to evaluate experimental data. Even then, the limitations are obvious, as in the case of K where the thermodynamic investigations are quite often inapplicable under field conditions. This is because, although a quasi-equilibrium in K exchange can be achieved in the laboratory, these conditions are seldom, if ever, attained under field conditions (Sparks,

1987). Agricultural soils are, for the most part, in a state of disequilibrium owing to both fertilizer input and nutrient uptake by plant root. It thus appears that a universal and accurate definition of a root's chemical environment awaits the proper application of thermodynamics for the root's ambient solution (Adams, 1974) or even kinetics, as in the case of K (Sparks, 1987), where thermodynamics has been found inadequate.

Soil extractions with different extractants provide a second approach in defining the root's chemical environment. This approach has been particularly successful in understanding cases like P insolubility, soil acidity, and K fixation. However, this approach also fails to define precisely the root's chemical environment. Though this approach also suffers from deficiencies, such as the extractants removing arbitrary and undetermined amounts of solid-phase electrolytes and ions (or the extractants causing precipitation of salts or ions from the soil solution) and the soil–plant interrelationship defined in terms of the solid-phase component of the soil, even though the solid phase is essentially inert except as it maintains thermodynamic equilibria with the solution phase (Adams, 1974), the latter part could be researched more to understand how the solid phase–solution phase equilibria can be interpreted to give a newer meaning to quantifying nutrient availability. It is in this context that the role of the plant nutrients' "buffer power" assumes crucial importance.

The close, almost linear, relationship in a low concentration range of <0.5 mM for $NO_3^- - N$, $NH_4^+ - N$, K^+, $H_2PO_4^-$, and HPO_4^{2-}, which has been established by numerous solution culture experiments, can be quantitatively described by the equation

$$U = 2\pi r \alpha C_r, \tag{8.1}$$

where U is the uptake of a 1-m root segment, r is the root radius, C_r is the concentration of the ion at the root surface, and α is the root absorbing power (Mengel, 1985). The metabolic rate of the root determines its absorbing power. A high root absorbing power would imply that a relatively high proportion of nutrient ions coming in contact with the root surface is absorbed and vice versa. The nutrient ion concentration at the root surface (C_r) depends on α since a high root absorbing power tends to decrease C_r; it also depends on the rate of movement from bulk soil toward the root (Mengel, 1985). Diffusion and/or mass flow controls this movement. But it is now established that nearly 95% of this movement for nutrients such as P, K, and Zn (among heavy metals) and, possibly NH_4^+, is by way of

diffusion. When root uptake of an ion species is less than its movement toward it, accumulation of the ion species on the root surface is bound to occur, as has been shown to be the case with Ca^{2+} where mass flow contributes to this accumulation (Barber, 1974). The diffusive path for ions, such as P and K, which plant roots take up at high rates but which are in low concentration in the soil solution near the root, is the concentration gradient. In a sense, the effective diffusion coefficient which quantifies the diffusive path and the buffer power are analogous because the diffusive flux across the root surface is integrally related to the nutrient buffer power. This has been shown to be true in the case of P where a highly significant positive correlation between the two was found to exist in 33 soil samples obtained from experimental sites in the United States and Canada (Kovar and Barber, 1988). However, in a routine laboratory setup, it is far easier to measure the buffer power than the effective diffusion coefficient and this review will further focus on the question of how buffer power can be quantified without recourse to cumbersome analytical techniques and how its integration into routine soil test data will considerably improve predictability of nutrient uptake.

3.2. Measuring the nutrient buffer power and its importance in affecting nutrient concentrations on root surfaces

The ability to predict the mobility of dissolved chemicals, such as fertilizers, in the soil is of considerable value in managing fertilizer applications. Soil testing, in its essence, aims to achieve this. While modeling transport and retention of ions from thermodynamic (Selim, 1992), kinetic (Sparks, 1989), and mechanistic (Barber, 1984) angles could be very informative, the importance of translating this information into practically feasible procedures in crop production calls for an understanding not only of the basic concepts but of their intelligent application as well. In a dynamic state of plant growth, the concentration of any nutrient on the root surface is nearly impossible to measure since both the nutrient in the plant tissue and the root absorbing power, which directly affects it, change quickly due to root metabolic processes. The inability of even mechanical–mathematical models to accurately predict nutrient influx rates has recently been highlighted (Lu and Miller, 1994). Hence, if an effective soil testing procedure is to be devised for a nutrient, which is an alternative to defining the plant root's chemical environment, one must resolve the problem of quantifying the nutrient concentration on the root surface indirectly, even if it is impossible to resolve it directly, for the reasons mentioned above.

Using Fick's first law,

$$F = -D(\mathrm{d}C/\mathrm{d}x), \tag{8.2}$$

where F is the flux, $\mathrm{d}C/\mathrm{d}x$ is the concentration gradient across a particular section, and D is the diffusion coefficient, Nye (1979) has suggested that the formula can be applied to both ions and molecules. The negative sign for D implies net movement from high to low concentration. Although for molecules in simple systems like dilute solutions D may be nearly constant over a range of concentrations, for ions in complex systems like soils and clays D will usually depend on the concentration of the ion, and on that of other ions as well (Nye, 1979). Nye (1979) has further suggested that though Fick's first law may be derived from thermodynamic principles in ideal systems, in a complex medium such as the soil, the above equation may be regarded as giving an operational definition of the diffusion coefficient. Thus, Nye (1979) defines the diffusion coefficient as

$$D = D_1 \theta f_1 (\mathrm{d}C_1/\mathrm{d}C) + D_\mathrm{E}, \tag{8.3}$$

where D_1 is the diffusion coefficient of the solute in free solution, θ is the fraction of the soil volume occupied by solution and gives the cross section for diffusion, f_1 is an impedance factor, C_1 is the concentration of solute in the soil solution, D_E is an excess term which is zero when the ions or molecules on the solid have no surface mobility, but represents their extra contribution to the diffusion coefficient when they are mobile. D_E can generally be neglected since only in rare instances will it play any role in diffusion of plant nutrient ions in soil (Mengel, 1985). From the point of view of nutrient availability, $\mathrm{d}C_1/\mathrm{d}C$, which represents the concentration gradient, assumes crucial importance, as we shall see below.

The term $\mathrm{d}C_1/\mathrm{d}C$, where C_1 is the concentration of the nutrient ion in the soil solution and C is the concentration of the same ion species in the entire soil mass, assumes considerable significance in lending a practical meaning to nutrient availability. If we ascribe the term "capacity" or "quantity" to C and "intensity" to C_1, we have in this term an integral relationship between two parameters that may crucially affect nutrient availability. Since the concentration gradient of the depletion profile of the nutrient in the zone of nutrient uptake depends on the concentration of the ion species in the entire soil mass (represented by "capacity" or "quantity") in relation to the rate at which this is lowered on the plant root surface by uptake (represented by "intensity"), it could be argued that a quantitative relationship between

Table 8.2 Comparison of P buffer power of eight widely differing central European soils (determined by two different techniques)

Soil	Regression (1)	Regression (2)	r (1)	r (2)
Benzheimer Hof	$Y=18.8x+7.94$	$Y=0.23x+8.98$	0.912	0.995
Hungen	$Y=38.2x-1.03$	$Y=4.32+0.25x$	0.967	0.997
Oldenburg B6	$Y=49.8x+0.52$	$Y=0.72+0.26x$	0.994	0.999
Wolfersheim	$Y=70.3x+0.03$	$Y=0.11+0.27x$	0.998	0.983
Obertshausen	$Y=70.5x+2.66$	$Y=2.89+0.30x$	0.966	0.998
Oldenburg B3	$Y=73.6x+2.07$	$Y=0.61+0.31x$	0.994	0.997
Klein–Linden	$Y=75.0x+0.38$	$Y=1.81+0.32x$	0.999	0.991
Gruningen	$Y=75.4x+0.89$	$Y=3.62+0.36x$	1.000	0.996

Notes: The b values in the regression functions represent the P buffer power of each soil. In regression function (1) (after Nair and Mengel, 1984) Y = CAL-P (Schüller's method) and in regression function (2) (after Nair, 1992a,b) Y = the author's method. x in both refers to electro-ultrafilterable P. Note the very high r values in all the cases. The soils are arranged in their sequential increase in P buffer power.

the two should represent the rate at which nutrient depletion and/or replenishment in the rooting zone should occur (Nair, 1984a,b). This relationship has been functionally quantified by Nair and Mengel (1984) for P in eight widely differing central European soils (Table 8.2) and the term dC_1/dC has been referred to as the "nutrient buffer power." Nair and Mengel (1984) used electro-ultrafiltration (EUF) to quantify C_1 while using an incubation and extraction technique to quantify C. For P, C was found to closely approximate isotopically exchangeable P (Keerthisinghe and Mengel, 1979), but in the experiments conducted by Nair and Mengel (1984), it was estimated by the extraction of incubated soil with an extractant which was a mixture consisting of 0.1 M Ca lactate + 0.1 M Ca acetate + 0.3 M acetic acid at pH 4.1. The extractant exchanges adsorbed phosphate and dissolves Ca phosphates except apatites; the method known as the "CAL-method," developed by Schüller (1969), is now widely used in central Europe. In the case of K^+ and NH_4^+-N, C denotes the concentration of exchangeable, and to some extent nonexchangeable, fractions (Mengel, 1985). Since very low concentrations in the range of 2.0 μM may be attained on the root surface for both P and K (Claassen and Barber, 1976; Claassen et al., 1981; Hendriks et al., 1981), Nair and Mengel (1984) had to use EUF to quantify C_1. Thus, the nutrient depletion around the roots which is

caused by the diffusive flux of the nutrients toward the root surface is related to both the quantity and the intensity parameters, and a quantifiable relationship between both represents the buffer power specific to the nutrient and the soil. A growing root will at first encounter a relatively high concentration of P which is in the range of the concentration of the bulk soil solution (Nair and Mengel, 1984). As uptake continues, a depletion will occur at the root surface. This depletion profile gets flatter with enhanced nutrient uptake (Claassen et al., 1981; Hendriks et al., 1981; Lewis and Quirk, 1967). But it is the capacity of the soil to replenish this depletion which ensures a supply of nutrient ions to the plant root without greatly depressing its average concentration on the root surface. It is the nutrient's buffer power that decides these depletion and/or replenishment rates. A soil with a high P buffer power implies that the P absorbed from the soil solution is rapidly replenished. In such a case, P concentration at the root surface decreases only slowly and mean P concentration at the root surface remains relatively high. In soils with a low P buffer power, the reverse is true, and P concentration at the root surface is rapidly diminished and remains relatively low. This has been proved experimentally for P (Nair, 1992a,b; Nair and Mengel, 1984). This phenomenon holds true for Zn^{2+} (Nair, 1984a,b), K (Nair et al., 1997), and $NH_4{}^+ - N$ as well (Mengel, 1985).

4. QUANTIFYING THE BUFFER POWER OF SOILS AND TESTING ITS EFFECT ON NUTRIENT AVAILABILITY

4.1. Phosphorus

When the exchangeable or desorbable nutrient ions are plotted on the y-axis and the corresponding concentration of the same ions in the equilibrated solution on the x-axis, we obtain a slope, the steepness of which represents the buffer power for that ion. The P buffer powers of eight central European soils widely differing in their physicochemical properties are reported in Table 8.2.

The "quantity" factor (C) in Eq. (8.3) was determined by two methods: (i) by an incubation and extraction technique (Nair and Mengel, 1984) and (ii) by an absorption–desorption equilibrium technique (Nair, 1992a,b) while the "intensity" factor (C_1) was determined by EUF (Nemeth, 1979). It is highly remarkable that the correlation coefficients, in the case of all the soils investigated, between C (represented by y) and C_1 (represented by x) are very highly significant as indicated by the r values, which in almost all cases were close to unity [including one soil (Gruningen) in which it was unity]. This clearly establishes the fact that the techniques employed will accurately

quantify the concentration gradient for P in the soils investigated when plants are grown in those soils. If this hypothesis is true, the impact of the P buffer power will clearly be reflected in the P uptake by the test plant since the P buffer power becomes the most crucial factor in predicting P availability. This can be tested by correlating P uptake with the routine soil test data without integrating the P buffer power and also by integrating the P buffer power. Nair and Mengel (1984) used the multiple linear regression equation $Y = a + bx + cz$, where Y = P uptake by the test plant, x = routine soil test data, z = P buffer power, and a and b = constants, to test the hypothesis. The impact of the P buffer power on P uptake vis-a-vis P availability is clearly shown by the data in Table 8.3.

In both cases of routine soil test data, the predictability of uptake was remarkably increased by integrating the P buffer power. The coefficient of determination, which is a measure of the precision of these computations, increased from 15% to 79% in the case of EUP-P and from 51% to 89% in the case of CAL-P. This in effect means that by integrating the P buffer power, the precision of P uptake predictability increased by 427% in the case of EUF-P and 74% in the case of CAL-P. Obviously, the increase has been very remarkable in the case of EUF-P. This also shows that the quantification of either the intensity factor alone (as in the case of EUP soil test data) or the quantity factor alone (as in the case of CAL soil test data) is insufficient to precisely predict P availability. A substantial proportion of the variance in P uptake is contributed by the P buffer power. From the above arguments, it follows that soils with a low buffer power for a particular nutrient requires a high initial concentration of the ions and vice versa. Mengel and Busch (1982) provided experimental evidence to substantiate this in the case of K^+ uptake of rye grass growing in nine soils of widely differing physico-chemical properties. This would also point to the fact that the relationship

Table 8.3 Correlation coefficients (*r*) for the relationship of P uptake versus routine P soil tests without (A) and with (B) integration of the P buffer power

	A	B
P uptake versus EUF-P	0.393*	0.8870**
P uptake versus CAL-P	0.714**	0.9415**

After Nair and Mengel (1984).

Notes: Electro-ultrafilterable P (EUF-P) and Ca lactate + Ca acetate + acetic acid mixture extractable P (CAL-P) (Schüller, 1969), respectively, used routinely to characterize P availability in central European soils.

*Significant at 5% confidence level.

**Significant at 1% confidence level.

between buffer power for the nutrient and the "critical" or "cut off" limit where plant yield is perceptibly reduced have an inverse relationship—a soil with a low buffer power for the nutrient resulting in a higher critical concentration in the plant tissue as compared to a soil with a relatively high buffer power having a lower critical concentration in the plant tissue for the same nutrient. This has been found in the case of K (Mengel and Busch, 1982) and P (Prabhakaran Nair, unpublished data). Prabhakaran Nair (unpublished data) found a very highly significant negative correlation between the plant top critical concentration for P and the P replenishment rate in the soil substrate which the P buffer power represents in summer rye (*Secale cereale* L.). In the case of dry matter yield this relationship was significant, but positive. This suggests that the P buffer power controls the P depletion and/or replenishment in the rooting zone and its accurate measurement would be the key to a precise quantification of P availability. Remarkably, the P buffer power of the soils had no direct relationship to clay or humus content, or soil pH (Nair and Mengel, 1984).

4.1.1 P buffer power measurement versus soil test P data for dependability of availability prediction

The important question on which the choice between P buffer power and/or contemporary or routine soil tests has to be made depends on what one aims to achieve inasmuch as prescriptive soil management practices are concerned. Contemporary soil tests are based on philosophies and procedures which were developed several decades ago, with essentially no change in the general approach. In order to be accurate, a soil test must measure both solution concentration of nutrients and their rates of movement through the soil. The "buffer power approach" seems to accomplish this. Virtually no soil test provides information about the most important factors which govern phosphate availability, which are phosphate concentration in the soil solution and the phosphate buffer power. In the widely used bicarbonate method (Olsen et al., 1954) or using water extraction (van der Paauw, 1971), the P quantities recovered may be 10–100 times more than that found in the soil solution (Mengel, 1985). Thus, all the methods which use an acid extraction extract much more phosphate from the "labile pool" (Larsen, 1967). Acid extractions, in certain instances, can also extract phosphate that under normal crop growth will be found unavailable to plant roots. The discrepancy between contemporary soil tests and crop response to P application has recently been highlighted (Nair, 1992a,b). In an extended study comparing eight central European soils with extremely differing physicochemical properties, Nair

(1992a,b) found that the response to a wide range of P application to summer rye grass (*S. cereale* L.) has no relevance at all to routine soil test data. Three routinely used soil tests, namely, the 0.01 M $CaCl_2$ test (Mattingly et al., 1963), the CAL-P test (Schüller, 1969), and the EUF-P test (Nemeth, 1979), were considered. The fluctuations in shoot P concentration with regard to P application were not at all reflected by the soil test values. Two of the soils which were at either extremes of "availability" (as characterized by the soil tests) showed totally divergent responses to P application, while the response was found to be very consistent considering the soil's P buffer power. This proves that the accuracy of routine soil tests can be vastly enhanced by integrating the corresponding P buffer power of the soil.

Buffer curves are extremely important in determining phosphate availability. The equilibration of a soluble fertilizer incorporated into a soil is not merely a question of adsorption and/or precipitation, but also of diffusion. Even if the fertilizer source is soluble and well mixed with the soil, the phosphate distribution is not homogenous, resulting in areas of high and low phosphate concentration. Since phosphate diffusion is a slow process, an even distribution brought about by diffusion takes time. The contact period between phosphate fertilizer and the soil has an impact on P availability, which has practical importance, and this can be depicted by buffer curves as shown in Fig. 8.1 (Barekzai, 1984). This figure represents on the *y*-axis

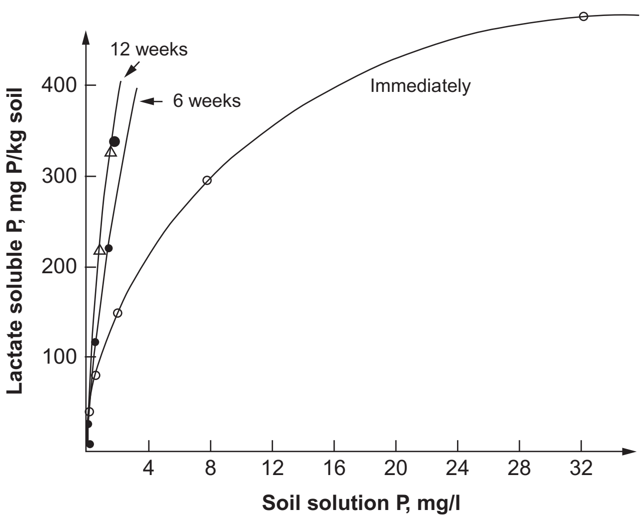

Figure 8.1 Phosphate buffer curves of an acid soil obtained immediately after phosphate application and 6 and 12 weeks after phosphate application. *After Barekzai (1984).*

P quantity (Ca lactate soluble) and on the *x*-axis P intensity (electro-ultrafilterable) and shows that the solubility of the applied P fertilizer decreased considerably during the 6 weeks of incubation as compared to the time immediately after application. In fact, these curves show the P aging process and reflect the phosphate concentration of the bulk soil solution. The steepness of the curve at a given phosphate concentration reflects the buffer power and this steepness for eight widely differing central European soils was quantified by computing a regression function between P quantity (Ca lactate soluble P) and P intensity (electro-ultrafilterable P); the *b* values in the regression functions were calculated to represent the P buffer power (Nair and Mengel, 1984). Considerable differences can be found among soils in their P buffer power; acid tropical soils invariably have a high buffer power, meaning that at a given quantity of available P, the P concentration of the soil solution is relatively low (Pagel and van Huay, 1976). With soils widely differing in their P buffer power, at an identical quantity of available P, the P concentration of the soil solution can differ by a factor of 100 (Barekzai, 1984).

4.1.2 P buffer power and Q/I relationship

Almost half a century ago Schofield (1955), while introducing the *Q*/*I* (quantity/intensity) concept to soil P, argued that the amount of P available to plants is not necessarily dependent on the size of the labile soil P pool and suggested that the work required to remove P from the labile pool might be crucial in determining the uptake of this element by plant roots. In fact, the P buffer power might be an indirect measure of the work required to remove P from the labile pool to affect plant uptake. There has been research on both sorption and desorption *Q*/*I* relationships (Raven and Hossner, 1994) and their theoretical representations are shown in Figs. 8.2 and 8.3. As soil P release is a key feature in P supply to plants, the study of P desorption *Q*/*I* characteristics might be more adequate than P sorption *Q*/*I* characteristics when evaluating plant available P and P buffer power of soils. P buffer power quantification by the sorption method would only be valid if both sorption and desorption curves overlap and if the proportion of solution P in the total desorbed P is negligible and all of the sorbed P is also desorbed (Raven and Hossner, 1994). The success of the adsorption–desorption equilibrium approach in quantifying exactly the P buffer power of eight widely varying central European soils (Nair, 1992a,b) lies in the above fact. However, P sorption and desorption *Q*/*I* curves generally do not coincide and sorption–desorption hysteresis is commonly observed

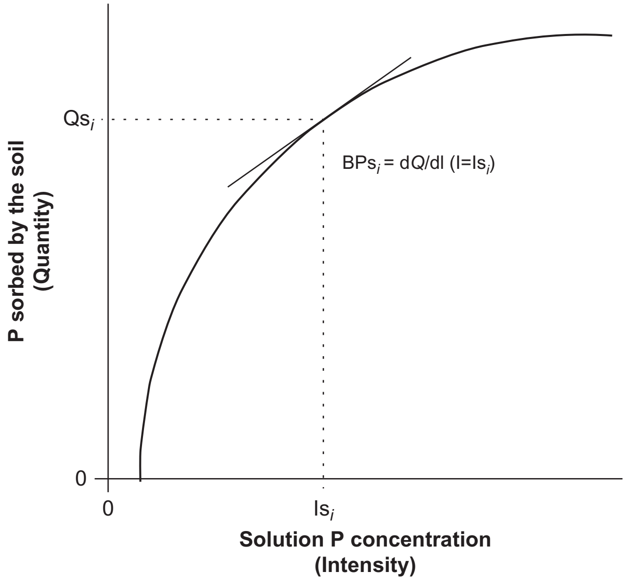

Figure 8.2 Theoretical soil P sorption curve and related parameters (Qs_i, amount of P sorbed by the soil in situation *i*; Is_i, solution P concentration in situation *i*; and Bps_i, P buffering power at Is_i). *After Raven and Hossner (1994).*

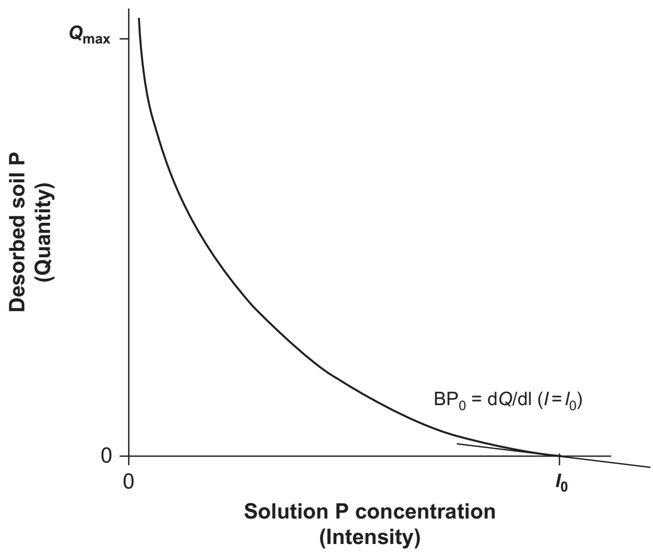

Figure 8.3 Theoretical soil P desorption *Q/I* curve and related parameters (Q_{max}, maximum desorbed soil P, labile soil P, or resin-extractable P at a 4/3 soil/resin weight ratio; I_0, solution P concentration when no P is desorbed or $Q = 0$; and BP_0, P buffering power at I_0). *After Raven and Hossner (1994).*

(Barrow, 1983; Fox and Kamprath, 1970; Okajima et al., 1983). However, P buffer power values derived from sorption curves appear to be adequate capacity indexes in terms of P uptake by plants (Bowman and Olsen, 1985a; Holford, 1988). The latter author, using results from 15 soils of diverse P characteristics, reported that the buffer capacities derived from P adsorption isotherms are satisfactory for characterizing P desorption, as well as adsorption, in the context of P diffusion in the soil and P uptake by plants. He further stated that during the later stages of P uptake, buffer capacities were always greater than indicated by adsorption measurements, suggesting that nonlabile P was making a significant contribution to the replenishment of the soil solution. Recent investigations (Raven and Hossner, 1994) indicate that P buffer power values derived from sorption *Q/I* curves differ from those of desorption *Q/I* curves. They have reported that test plant P uptake (in this case a single corn plant in a short-term container culture) was better related to the quantity parameter derived from the desorption *Q/I* relationship (Q_{max}) as shown in Fig. 8.4. Fox and Kamprath (1970) developed a standard procedure to determine sorption curves that allow computation of the quantity of P fertilizer required to establish a desired P concentration in the soil solution. Though Beckwith (1965) tentatively suggested that adjustment to 0.2 mg P/l would be adequate for successful growth of most plants, these critical values would depend on plant

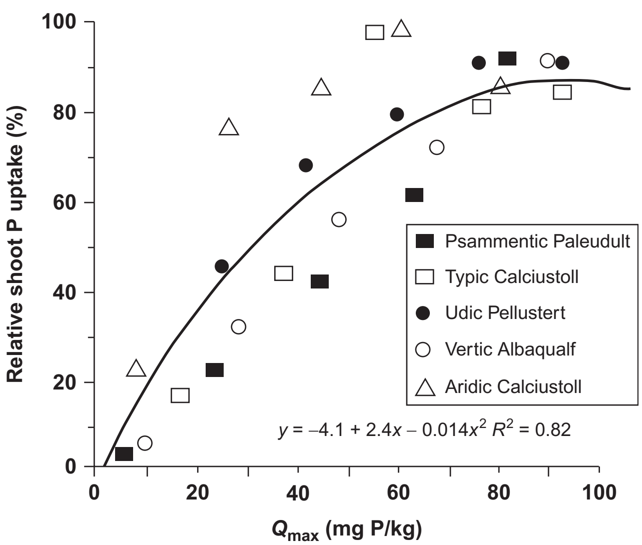

Figure 8.4 Relationship between the relative shoot P uptake of corn plants and the maximum desorbed soil P (Q_{max}). *After Raven and Hossner (1994).*

species and nutritional factors (Fox, 1981). Further, recourse to merely a critical solution P concentration value would neglect P buffering effect. Procedures evaluating buffering capacities of soils are often time consuming, but the question as to the need for precise documentation of soil parameters quantifying P uptake with precision for field crops, where other important factors may come into play, cannot be underestimated. Empirical correlations based on Mitcherlich-type equations have been fairly successful in extension work, but these equations are restricted to areas with similar soil, climate, and management. Since these equations cannot accommodate soils of divergent phosphate buffering capacities, the need to include a numerical value for P buffering capacity can hardly be overlooked (Bowman and Olsen, 1985b). The usefulness, for field application, of Q/I relationships obtained in the laboratory is often questioned. Q/I relationships can give an idea of the relative ease with which the "readily extractable P" will be released (buffered)—something that other conventional soil testing procedures do not give (Bowman and Olsen, 1985b). Estimates can be made of the number of years the soil can supply P before deficiency levels set in. Hence, the interpretation of soil tests for soils of identical Q but with a higher P buffer power will need to be different. Another important question is whether it is critical to employ laboratory desorption isotherm procedures merely because the procedure more realistically simulates plant uptake (Bowman and Olsen, 1985b). The scientific understanding of the uptake process seems more appropriately explained by the desorption isotherm process since plant uptake is basically a desorption process. However, Bowman and Olsen (1985b) suggest that where field responses are concerned, adsorption isotherms are more appropriate to standardize P buffer power of soils. The work of Nair and Mengel (1984) and Nair (1992a,b) suggests that both adsorptive and desorptive procedures are appropriate, the crucial question being how accurately these processes are determined in the laboratory and by plant culture techniques.

CASE STUDIES FROM ASIAN SOILS

4.2 Potassium

As discussed earlier with regard to P, the dynamics of K availability follows the same pattern as that of P, especially in the range of low concentrations. Beckett (1971) has used the activity ratio for K^+ and Ca^{2+} to determine K availability. Since interlayer K would play an important role in K availability, it would be

more logical to consider K buffer power in determining K availability. Routinely, it is the ammonium acetate extractant that is widely used to characterize K availability. The reason that this may not be suitable to characterize exchangeable K is that in the routine extraction, only the top layer is extracted, while interlayer K from which deep-rooted plants can feed is ignored (Nair et al., 1997). There is extensive evidence to substantiate this (Mengel, 1985). The importance of interlayer K in the nutrition of deep-rooted and perennial crops, such as cardamom (*Elettaria cardamomum* M.), the world's most valuable spice crop, has been highlighted recently by Nair et al. (1997).

4.2.1 The importance of K buffer power determination in predicting K availability to perennial crops

As in the case of P, the K buffer power assumes great importance in predicting K availability, especially with regard to deep-rooted and perennial crops. With annual or biennial crops, K availability has been studied with reference to the exchangeable K. However, with perennial and deep-rooted crops nonexchangeable and interlayer K play a crucial role in K availability. Three soil parameters that control the rate of K supply to plant roots which have been used for predicting K absorption by plants are the K intensity in the soil solution, the K buffer power, and the effective diffusion coefficient (Beckett, 1971; Claassen et al., 1986; Mengel and Kirby, 1980). K buffer power can be directly obtained from the K quantity–intensity relationship. The effective diffusion coefficient depends on, among other factors, the buffer power. Plants feed not only from exchangeable K but also from nonexchangeable K^+, which mainly consists of K^+ trapped in the interlayers of nonexpanded 2:1 clay minerals (Hoagland and Martin, 1933; Schachtschabel, 1937).

Exchangeable K comprises that which can be exchanged with the ${NH_4}^+$ ion, and is primarily planar K^+, the interlayer K^+ of expanded 2:1 clay minerals and some of the K^+ at the interlayer edges of nonexpanded 2:1 clay minerals. Interlayer K^+ of nonexpanded clay minerals such as illites and interlayer and lattice K^+ micas (present in feldspars) constitutes the nonexchangeable K^+. The interlayer K^+ is of particular importance in the nutrition of deep-rooted and perennial crops such as cardamom, as demonstrated by the recent work of Nair et al. (1997), and also for annual crops such as rye grass (*Lolium perenne* cv. Taptoe) (Mengel and Uhlenbecker, 1993).

In most of the soil tests for K^+ availability, nonexchangeable K is not considered. For cereals such as wheat (*Triticum aestivum*) 80% of the K^+ extracted by the crop came from the nonexchangeable K pool. This is one of the most important reasons for the poor soil test crop response relationship with regard to K fertilizer application based on such tests

(Kuhlmann and Wehrmann, 1984). The contribution of nonexchangeable K to plant availability was assessed by 1 M HCl extraction by Schachtschabel (1961), similar to the 1 M HNO_3 extraction proposed by Pratt (1965) and McLean and Watson (1985). However, the efficiency of 1 M HCl extraction to quantify plant available K from the nonexchangeable pool has been disputed (Boguslawski and Lach, 1971; Grimme, 1974; Kuhlmann and Wehrmann, 1984). Soils containing primarily 2:1 clay minerals such as vermiculite and illite have interlayer K in excess of crop demand. However, the availability of interlayer K of nonexpanded minerals is independent of the quantity of interlayer K as such, but dependent on its release rate depending on the type of K^+ bearing minerals (Sparks, 1987). Release of K from interlayer positions is an exchange and diffusion process (von Reichenbach, 1972). While exchange depends on the cation species and their concentration near the surface of the mineral, diffusion depends largely on the expansion of the mineral and therefore on soil moisture. Net release of K will only occur if the K concentration of the adjacent solution is low (Mengel, 1985). Martin and Sparks (1983), while studying the release of nonexchangeable K^+ from sandy loam and loamy sand extracted with a H^+ charged ion exchanger resin, found large release of K^+ with a K^+ concentration of about 1–2 μM in the contact solution. This concentration may approximate the rhizosphere concentration level. Under submerged conditions as in rice, there can be a depletion zone for K in the rhizosphere (Xu and Liu, 1983). Plant roots act as a sink for K and maintain the K solution concentration at very low levels (Kuchenbuch and Jungk, 1984); this would cause further release of interlayer K (Mengel, 1985). These considerations point to the important fact that a precise quantification of K availability, where nonexchangeable interlayer K is concerned, hinges primarily on its release rate, which the K buffer power attempts to quantify, as we shall see in the following discussion.

Nair et al. (1997) selected cardamom (*E. cardamomum* M.) to demonstrate the importance of nonexchangeable and interlayer K on K availability vis-a-vis the K buffer power. The K buffer power curves were constructed by a two-step extraction in which 1 N HNO_3 was used to determine the quantity of K (Wood and De Turk, 1941) and 1 N NH_4OAc was used to determine K intensity. The NH_4OAc extractant is universally used to determine exchangeable K. The contribution of nonexchangeable K to plant availability has been assessed both by extraction with 1 M HCl (Schachtschabel, 1961) and 1 M HNO_3 (McLean and Watson, 1985; Pratt, 1965). Nair et al. (1997) regressed 1 N HNO_3 extractable K (y) over 1 N NH_4OAc extractable K (x) to obtain the K buffer power (Table 8.4 and Photo 8.1).

Table 8.4 K buffer power of cardamom-growing soils from two regions of southern India extensively growing this crop

Region	Regression function ($Y = a + bx$)	r	Crop yield (kg/ha)
Coorg	$142.38 + 1.4443x$	0.8561*	155
Idukki	$592.46 + 0.9172x$	0.5799**	80

After Nair et al. (1997).
Notes: *b* values in the regression function represent the K buffer power of the soil. The K buffer power refers to pooled values of soil samples obtained from 94 locations covering an area of more than 20,000 ha in the two cardamom-growing regions of southern India, namely, Coorg and Idukki. Yield data refer to the same locations.
*Significant at a confidence level of 1%.
**Significant at a confidence level of 5%.

Photo 8.1 Base of the cardamom plant (India).

Data in Table 8.4 clearly indicate that the Coorg soils, which had a much higher K buffer power, produced cardamom yield which was twice that obtained in the Idukki soils. The higher K buffer power of the Coorg soils was clearly reflected in the cardamom yield. By comparison, the 1 N NH_4OAc extractable K had no significant relationship with leaf K (Table 8.5) and further the integration of K buffer power with the routine soil test K data (NH_4OAc extractable K) remarkably improved this relationship.

Cardamom is a heavy feeder of K, and in India, which grows most of this valuable spice crop, and in other countries on the Asian and African continents where this crop is grown, its K fertilizer needs are almost always based on the exchangeable K determined by 1 N NH_4OAc. Data in Table 8.5 unequivocally show the inability of this extraction to precisely predict

Table 8.5 Correlation coefficients and regression functions for the relationship leaf K (*Y*) versus exchangeable K (*x*, NH_4OAc extraction)

Details	Regression function ($Y = a + bx$)	Correlation coefficient (*r*)
Leaf versus exchangeable K	Coorg $Y = 1.2701 + 0.0004$	0.2064
Leaf versus exchangeable K	Idukki $Y = 1.6448 + 0.000006$	−0.006

Notes: The correlation coefficients refer to the leaf samples from 94 locations from which soil samples were also obtained to calculate the K buffer power. In cardamom, the fifth pair of leaves from the top of each panicle bearing tillers are sampled for K analysis.
After Nair et al. (1997).

Table 8.6 Correlation coefficients (*r*) for the relationship between leaf K (*Y*) and exchangeable K (*x*, NH_4OAc extraction) for the pooled data (94 locations) from two regions (Coorg and Idukki) without (A) and with (B) K buffer power integration

Details	Correlation coefficient	
	A	B
Leaf versus exchangeable K	0.2510	0.4367**

**Significant at 1% confidence level.
After Nair et al. (1997).

K availability; further, data in Table 8.6 show how the situation is remarkably improved by the integration of the K buffer power into the computations. A substantial variation (302.7%) in leaf K is attributable to the K buffer power. These results have been obtained from a very extensive area (more than 20,000 ha), which demonstrates their significance (Photo 8.2).

The K buffer power in this instance integrates both exchangeable (NH_4OAc extraction) and nonexchangeable and/or interlayer K (HNO_3 extraction) and this gives an accurate measurement of K depletion around the plant roots. In a recent study (Mengel and Uhlenbecker, 1993) on K availability from interlayer K to rye grass (*L. perenne* L.cv. Taptoe) it was observed that the rate constant (*b* values) obtained by correlating K released (from the interlayers of clay minerals) and time periods by a modified EUF technique was closely related to K uptake and represented the K availability index from nonexchangeable K. These rate constants, according to the authors, are of the utmost importance because they provide information on the availability of nonexchangeable K in attaining maximum yield; and a set of "critical *b*" values toward attaining this objective have been reported. It appears that the rate constants of Mengel and Uhlenbecker

Photo 8.2 Effect of K fertilizer application in cardamom based on K buffer power of the soil in Karnataka State, India.

(1993) are analogous to the K buffer power values reported by Nair et al. (1997), because, though the techniques differ in their details, they have accomplished the same objective of precisely predicting K availability from the nonexchangeable pool and/or the interlayer K. The capability of tapping interlayer K varies among plant species. For instance, Steffens and Mengel (1979) found that rye grass (*L. perenne*) could feed from interlayer K^+ for a longer period without yield depression, while red clover (*Trifolium pratense*) could not. These authors reported that since *L. perenne* had a longer and deeper root system compared to *T. pratense*, the former could grow satisfactorily while relatively low K^+ concentration at which the latter would already suffer from K deficiency (Steffens and Mengel, 1981). The differences in root mass, root length, and root morphology between monocots and dicots explain the better K^+ feeding capacity from interlayer K^+ of the former compared to the latter (Mengel, 1985).

Cotton, *Gossypium hirsutum* L., is another deep-rooted long-duration crop, on which the K buffer power exerts considerable influence on K acquisition. Brouder and Cassman (1994) evaluated K uptake by cotton in a vermiculitic soil using mechanistic models and observed that initial model output produced both substantial under- and overpredictions of whole-plant K accumulation. Model predictions were greatly enhanced by estimating the K buffer power. They further concluded that the contribution of the fixed K pool to the plant available K pool was likely to be substantial and that this influence must be captured in estimates of the soil K buffer power. These studies were conducted after observing in a San Joaquin Valley cotton field in

California that cotton exhibited late season K deficiency while other crop species remained unaffected. In such cases, the precise estimation of K buffer power will lead to far more dependable K fertilizer recommendations than estimations by the routine NH_4OAc extraction.

Though it has long been recognized (Schachtschabel, 1937) that the soil K fraction which is not exchangeable by NH_4 ions (nonexchangeable K) may be important for the supply of K to plants, it is only of late that researchers have paid more attention to this aspect. The work of Sparks and Huang (1985) has very carefully examined the release mechanism from the nonexchangeable source and the factors controlling it. Considerable portions of initially nonexchangeable K can be utilized by plant roots even within a few days (Kuchenbuch and Jungk, 1984). The depletion zone, however, extends into the ambient soil for 2 mm only. Hinsinger et al. (1992) embedded phlogopite in agar and observed that the interlayer K of this mineral was entirely lost in the close vicinity of ryegrass roots within 4 days. Since the process limiting the rate of K uptake in the rhizosphere may be K transport through the soil rather than the release from minerals as such, some researchers have focused their attention on this aspect. One such example is the mechanistic mathematical model of Claassen and Barber (1976). Claassen et al. (1986) and Claassen (1990) have successfully applied the model referred to above to predict K depletion profiles in soil around plant roots. Quite recently, Meyer and Jungk (1993) have used these models to predict K uptake by test plants from exchangeable and nonexchangeable K sources. They reported that 64–79% of the K taken up by wheat (*T. aestivum* L.) and sugar beet (*Beta vulgaris* L.) was derived from the rapidly released exchangeable and 21–36% from the nonexchangeable or less mobile soil K fraction.

The buffer power describes the relationship between adsorbed K and the K concentration of the ambient solution. In simulation models it is assumed that this relationship is linear and hence independent of soil solution concentration. However, in desorption studies with soil a sharply curved buffer relationship could be found and Meyer and Jungk (1993) have referred to it. Very near the plant roots the soil can be subjected to a curved buffer function since plant roots strongly reduce the soil solution concentration.

An important aspect to be considered in the utilization of nonexchangeable K is the role of plant roots. Plant species differ in their ability to utilize nonexchangeable K and this has been attributed to the differences in root length (Mengel and Steffens, 1985). Radial distance between two single roots decreases, consequently increasing root density and this would result in the overlapping of the depleted soil volumes between these roots.

This would also lead to a decrease in rate of K uptake per unit root. In the case of the rapidly diffusing K fraction, which has a higher mobility, the competition effect between roots could be very intense. There is evidence to support this view, as shown by the work of Mitsios and Rowell (1987), who observed that the contribution of nonexchangeable K increased with a corresponding increase in root density. Additionally, the differences in root hair length and density among plant species (Föhse et al., 1991) affect their ability to acquire soil K. Accordingly, the work of Meyer and Jungk (1993) has shown that K uptake was higher when they included root hairs as well in their model calculations. Since root hairs contribute to an increase in root absorbing surface, a reduction in the distance of diffusion from the site of K release to the site of K uptake, and an increase in the K concentration gradient, they can be expected to exert a pronounced effect on K availability from the less mobile K fraction.

4.2.2 The commercial significance of K buffer power determination in K fertilizer management for perennial crops

The commercial significance of K buffer power determination for dependable K fertilizer recommendations assumes great importance in those countries which are faced with importing these fertilizers at a huge cost to the national exchequer. India is a case in point. The recent decontrol of prices of both phosphate and potassium fertilizers by the government of India resulted in an overnight escalation of their market prices. In a situation like that, the farmers become extremely wary of their field use and unless the fertilizer application is cost-effective, faith in their use, especially those mentioned above, would be shattered.

The K fertilizer recommendation for cardamom has been based exclusively on NH_4OAc extraction. The investigation of Nair et al. (1997) showed its ineffectiveness. Though the importance of K buffer power in predicting K availability has been reported earlier, these research reports related mainly to annual crops such as white clover (During and Duganzich, 1979) and rye grass (Mengel and Busch, 1982); the work of Nair et al. (1997) was the first of its kind in perennial crops.

4.2.3 The role of the NH_4^+ on K^+ availability

One of the frequent assumptions made in predicting K availability in soils is that results from binary (two-ion) exchange systems can be extrapolated to ternary (three-ion) systems using appropriate equations. The K–Ca exchange reactions in soils are often investigated in laboratory studies. Most

of the research carried out on soil clay minerals and soils as exchanger surfaces (Argersinger et al., 1950; Gapon, 1933; Jardine and Sparks, 1984; Sposito, 1981a,b; Sposito et al., 1981, 1983; Vanselow, 1932) are binary exchange systems. However, field soils are at least ternary systems (Adams, 1971; Curtin and Smillie, 1983). The evaluation of soils as binary systems implies that these reactions can be used to predict results in ternary systems such as field soils. For this assumption to be valid, the binary exchange selectivity coefficients need to be independent of exchanger-phase composition (Lumbanraja and Evangelou, 1992). But, the work of Shu-Yan and Sposito (1981) showed that it is impossible to predict exchange phase–solution phase interactions in a ternary system such as the field soil from a binary system such as the laboratory sample. This focuses the importance of the ternary systems. As far as K availability is concerned, it would be important to include the NH_4^+ ion as well. The work of Lumbanraja and Evangelou (1992) has shown that K^+ adsorption to soil surfaces is suppressed in the presence of added NH_4^+, while the adsorption of NH_4^+ to the same surface is enhanced in the presence of added K^+. These observations point to the influence of added NH_4^+ on the desorption potential (chemical potential) of adsorbed K or vice versa (Lumbanraja and Evangelou, 1992) and would be relevant to the determination of K buffer power especially when agents containing NH_4^+ ions, such as NH_4OAc, are used in determining K buffer power (Nair et al., 1997). The work of Lumbanraja and Evangelou (1992), though, clearly demonstrates the effect of the NH_4^+ ion on K^+ desorption, with an increase in K^+ desorption in the presence of added NH_4^+. In its absence, it might be safe to conclude that the shape of the K buffer power curve will not appreciably change even if larger quantities of K are removed due to cropping and therefore can be considered as a relatively constant property of soils. There is evidence to support this view. These authors, while investigating the Q/I relationship on K uptake by wheat (*T. aestivum*) in calcareous vertisols and inceptisols of southwestern Spain, found that 80% of the K extracted came from the nonexchangeable K pool.

These observations, coupled with the ones discussed earlier, suggest that the precision of predicting K availability can be substantially enhanced by first quantifying the K buffer power of the soil in which the crop is intended to be grown. Admittedly, the rate-limiting steps involved in K dynamics are not entirely understood (Sparks, 1987). Notwithstanding this limitation, if one must move forward in devising better management of K fertilizers in crop production, a starting point has to be made with regard to precisely quantifying K availability. Quantifying the K buffer

power of soils and basing K fertilizer recommendations on this seems to be the best starting point.

4.2.4 K buffer power measurement versus contemporary soil test K data for dependability of K availability prediction—The context of MYR and MEY approaches

The importance of K buffer power determination in devising effective K fertilizer recommendations must be viewed against the twin objectives of maximizing fertilizer use efficiency to attain high crop productivity—the crucial concern of developing countries—and minimizing nutrient loss to the environment—the crucial concern of industrialized countries. Potassium losses are primarily due to leaching and occur on coarse-textured soils under humid conditions (Mengel, 1985). Where such leaching losses are acute, split application of K fertilizer adjusted to the crop demands and to the fluctuating weather conditions are considered a useful measure to enhance efficiency of K use by crops. Despite the fact that predictive kinetic models of K dynamics are absent and the K rate-limiting steps are still inadequately understood (Sparks, 1987) (a better understanding would doubtless result in better prediction of the fate of applied K and, consequently, assist in enhancing crop yields and K uptake efficiency, through more effective K fertilizer recommendations), the K fertilizer recommendations still continue to revolve around quantifying available K, mostly by standard extractions with NH_4OAc or acids such as 1 N or 1 M HNO_3 or 1 M HCl. A case in point is the MYR (maximum yield research) or MEY (maximum economic yield) approach. The recent findings of Narang et al. (1994) in India indicate that in a rice–wheat rotation of five crop seasons, the decline in available K was 12.3 μg/g at 120–30–30/120–60–30 (N–P–K rates) and 15.6 μg/g at 180–30–30/180–60–30 (N–P–K rates) over their respective initial levels, pointing out the anomalous and inconsistent fact that at identical K application rates the reduction in available K is variable. Obviously, such a conclusion is subject to scrutiny from the viewpoint both of quantifying available K (in this case the standard NH_4OAc extraction was employed) and of the varying N and P rates where interaction between the three nutrients (N, P, and K) is bound to play a role in their individual availability. However, one cannot ignore the inadequacy of such approaches, because these contemporary soil tests fail to detect precisely the differences in soil K availability. Contradictory results have been obtained where higher K fertilizer application resulted in a corresponding higher available K (Narang and Bhandari, 1990; Roy et al., 1990; Singh

and Nambiar, 1986) while the same practice resulted in a decline of extractable K (Hegde and Dwivedi, 1992; Swarup and Singh, 1987). Obviously, these inconsistent results cast a deep shadow of doubt on the dependability of contemporary soil tests for K availability in soils. A similar situation prevails in the case of rice production for MEY in Costa Rica. Using a modified Olsen's extractant, a mixture of $NaHCO_3$ + EDTA, Cordero and Espinosa (1994) classified soil K critical levels as low (<0.1 $cmol_c$/l), medium (0.11–0.2 $cmol_c$/l), and high (>0.2 $cmol_c$/l). The K critical level was set at 0.1 $cmol_c$/l and the K fertilizer recommendations varied from 30 to 60 kg K_2O/ha. But responses to K fertilizer up to 80 kg K_2O/ha were obtained even in soils with a K critical level of 0.15 $cmol_c$/l in vertisols and mollisols with high Ca + Mg contents (Cordero and Espinosa, 1994) indicating that the K critical level based on the soil extraction is not a dependable index of availability and the situation can vary from one soil to another. The above situation would call for different K fertilizer recommendations for different soils based on extractable K and the Ca + Mg/K ratio. This disallows K fertilizer recommendations in a universal manner. These are not the limitations which the K buffer power approach suffer from. Since the K buffer power quantifies the average K concentration on the plant's root surface, though indirectly (Nair, 1984a,b), it would provide greater precision in K availability prediction and, hence, result in more dependable and uniform K fertilizer recommendations. The supportive evidence provided by During and Duganzich (1979), Mengel and Busch (1982), Mengel and Uhlenbecker (1993), and Nair et al. (1997) reinforces this assumption. The MYR approach focuses on the BMP (best management practice) and aims to maximize crop yields wherever possible. Yet some of the key inputs, such as decisions on fertilizer rates, are still based on contemporary soil tests based on philosophies and procedures developed several decades ago with essentially no change in the general approach. In an interesting paper entitled "Maximum Yield Research: Friend of the Environment," presented at the 15th World Congress of Soil Science in Acapulco, Mexico, makes a strong case for this approach in maximizing crop production. He cites Borlaug (1990) the Nobel Peace Prize Winner, and Borlaug and Dowswell (1993) who said,

> *The only way for agriculture to produce sufficient food to keep pace with population and to alleviate the hunger of the world's poor is to increase the intensity of agricultural production under those ecological conditions which lend themselves to intensification while decreasing the intensity of production in the more fragile ecologies. Most of the yield increase in food production needed over the next*

> *several generations must be achieved through yield increases on land now under cultivation. Moreover, these yield increases must be achieved through the application of technology already available or well advanced in the research pipeline. This will not only lead to economic development but it will also do much to solve the serious environmental problems that come as a consequence of trying to cultivate lands that are not suited for crop production. Fortunately many of the more-favored agricultural lands currently under cultivation are still producing food at yield levels far below their potential.*

He further cites Cassman (1990) who mentions that the greatest challenge to global food output is

> *to understand how soil fertility management affects soil quality, and to apply this knowledge to integrate all aspects of crop management to optimize yield and input utilization efficiency over the long term. Soil fertility management governs plant nutrition, which in turn influences susceptibility to disease, plant growth and yield.*

In a nutshell, the MYR approach lays great stress on nutrition, yet the nutrient management aspects move along the beaten track. Unless imaginative attempts are made to revise the basic concepts of quantifying nutrient availability, even the MYR approach is bound to falter as has been clearly shown in the case of K recommendations for rice–wheat rotations in India and rice production in Costa Rica. These are but a few examples which have been reported and are reviewed here, and yet there could be many more which are not reported and which are outside the purview of this review. These facts call for a new direction in soil testing for nutrient availability. The Buffer Power Concept appears to provide this. The field experience of this new approach is detailed in the book "The Spirit of Enterprise—The 1993 Rolex Awards" which summarizes the work of Nair (1992a,b) in the farmers' fields in the Republic of Cameroon.

4.2.5 K buffer power and Q/I relationship

The use of the Q/I relationship to describe the K status of soils is based on Woodruff's (1955a,b) observations that K availability to plants can be characterized by the free energy of K–Ca exchange with regard to solid–solution reactions. Beckett (1971) listed a number of assumptions as prerequisites for Woodruff's observation to be valid. An important assumption is that the rate of K uptake by plant root must be regulated by "the difference in the equivalent free energies of K and Ca as offered to the uptake sites." Maas (1969) has provided experimental evidence to substantiate this from uptake data of excised maize roots. These data demonstrate that Ca^{2+} uptake in the

presence of K^+ is a competitive process. The rate of K uptake was maximized in the ΔG range predicted by Woodruff (1955b). Such experimental evidence of K uptake by excised maize roots provides supportive proof to the validity of Woodruff's observation that K availability could be described by the free energy of K–Ca exchange as long as all other soil factors related to plant growth are not limiting and are held constant (Beckett, 1972). The use of Q/I in predicting K availability to plants in soils has been widely tested (Beckett, 1972; Bertsch and Thomas, 1985). However, it has been shown that the Q/I relationship does not enjoy universal acceptance since a single relationship for all soils between K uptake by a given crop and AR_K does not exist, perhaps due to the nature of the soil components regulating AR_K (Evangelou et al., 1994) (Fig. 8.5). The reader is advised to read the excellent review of Evangelou et al. (1994) for a better appreciation of the new developments and perspectives on soil K Q/I relationships. The reasons for the failure of the Q/I concept to precisely predict soil K availability in all soils are varied and an important aspect that has to be recognized is that Q/I concept does not deal with physiological effects, but appears to be influenced by them (Evangelou et al., 1994). Mengel and Busch (1982) conducted an

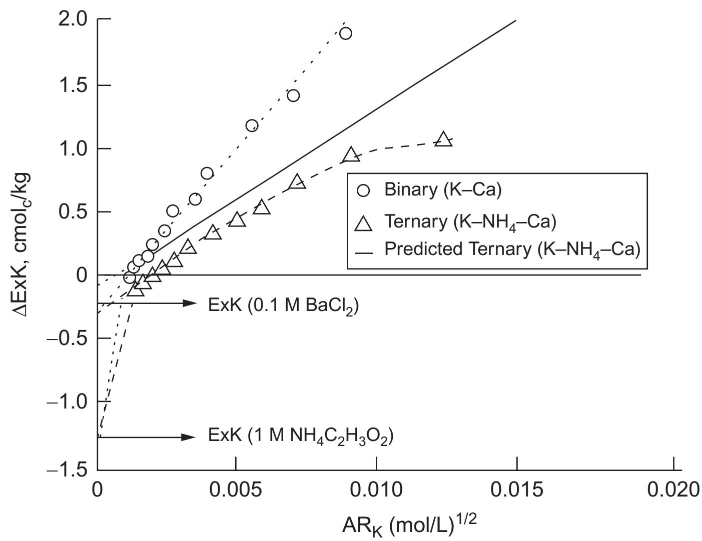

Figure 8.5 Potassium quantity/intensity (*Q/I*) plots of Eden soil in the absence (binary) and the presence (ternary) of NH_4 [ternary prediction is from experimental binary Vanselow exchange selectivity coefficients for K–Ca and NH_4–Ca exchange, and from experimental ternary activity ratios (AR) for K and NH_4; ExK is exchangeable K]. *After Lumbanraja and Evangelou (1990).*

interesting investigation dealing with some of these physiological effects. They demonstrated that a very close correlation ($r^2 = 0.908$), reflected by a parabola ($y = c/x$; Figs. 8.6 and 8.7), existed between K buffer power and the critical K^+ concentration of the soil solution. They estimated the K buffer power by correlating exchangeable K (0.2 N $BaCl_2$ exchangeable) as *y* (K, quantity) with soil solution K (electro-ultrafilterable) as *x* (K, intensity), and the *b* values in the regression functions were taken as a measure of the K buffer power. Nine central European soils of extremely differing natures were tested for K availability to a test crop of *Lolium multiflorum* (cv. Avance). These authors reported that as the K buffer power increased, the critical K concentration (the critical K concentration defined as that level below which a yield increase is obtained when K fertilizer is applied) decreased.

Though the *Q/I* concept does not deal with physiological effects, the latter influences it. For a better appreciation of the *Q/I* concept vis-a-vis the K buffering effect on prediction of K uptake, one should be quite familiar with plant nutrition concepts. Even if nutritional effects are assumed to play only a limited role in K uptake under a well-defined experimental setup, the ability of a soil to replenish K^+ in the soil solution must be considered a highly complex process and not solely dependent on K–(Ca + Mg) exchange alone (Evangelou et al., 1994). K availability is also controlled

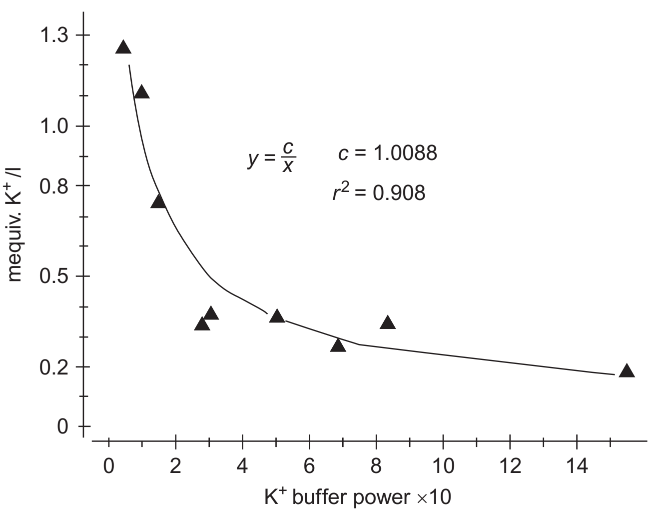

Figure 8.6 Relationship between the critical K^+ concentration of the soil solution and the K^+ buffer power: y = critical K^+ concentration; $x = K^+$ buffer power. *After Mengel and Busch (1982)*.

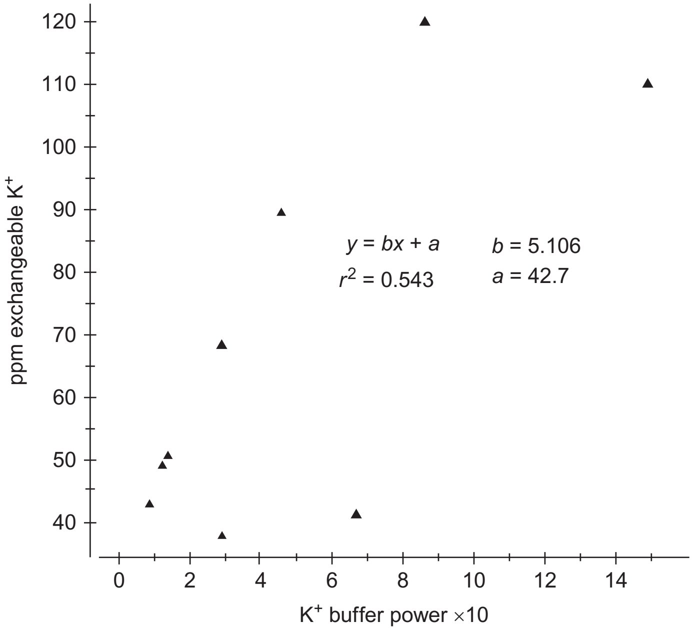

Figure 8.7 Relationship between the critical level of exchangeable K^+ and the K^+ buffer power: y = critical level of exchangeable K^+; x = K^+ buffer power. *After Mengel and Busch (1982).*

by additional factors, such as hysteresis or exchange irreversibility effects, anion effects, multiplication effects, potential-determining ion effects, and kinetic effects (Evangelou et al., 1994). To predict K availability with precision, these factors need to be further scrutinized. But, most importantly, it is the soil/soil solution–plant root surface interactions which merit closest scrutiny in predicting K availability. The importance of K buffer power has to be examined in this context. Since the ultimate objective in perfecting prescriptive soil management practices with regard to K fertilizer application, vis-a-vis soil testing for plant available K, hinges on the soil/soil solution–plant root interactive effects, and also since plant root surface K concentration during the dynamic state of plant growth is nearly impossible to measure in a field soil, Nair (1984a,b) has argued that a precise quantification of K buffer is an important prerequisite to accurately predict K availability and must be considered as such as an indirect measure of the plant root surface K concentration. The experimental evidence provided by Mengel and Busch (1982) and Nair et al. (1997) substantiates this view.

5. THE ROLE OF EUF IN MEASURING P AND K INTENSITY FOR THE CONSTRUCTION OF BUFFER POWER CURVES

In the construction of the buffer power curves it is imperative that both the quantity and the intensity factors are measured accurately. While the former can be quantified by an incubation and extraction technique (Nair and Mengel, 1984) or an adsorption–desorption equilibrium technique (Nair, 1992a,b), the precise determination of the latter poses greater problems. Here, the role of EUF in quantifying the intensity factor is briefly discussed. EUF is a flow and batch technique combined to determine the kinetics of K availability (Nemeth, 1971, 1979). It combines electrodialysis and ultrafiltration. Originally EUF was used to purify colloidal suspensions (Grimme, 1979) but it was later modified by Kottgen and Diehl (1929) for soil testing purposes. These authors attempted to extract the labile fraction of the plant nutrients without a chemical treatment such as chemical extraction. The EUF method eliminates accumulation of reaction products in the electrode compartments, and also charge on membranes separating the compartments as well as the effect of electroosmosis (Grimme, 1979; Nemeth, 1972). Nemeth (1971, 1972) modified the procedure to extract soil at three field strengths instead of one as done originally. Thus, an extraction (desorption) time of 10 min at 50 V and 20 °C was followed by two sequential extractions of 10 min each at 200 V and 20 °C and five sequential extractions of 5 min each at 400 V and 80 °C. The extraction period can be modified for different time sequences. For instance, Nair and Mengel (1984) collected three fractions, EUF-I + EUF-II, extracted at 200 V and 20 °C for 30 min and EUF-III extracted at 400 V and 80 °C between 30 and 35 min, in the case of P, while Mengel and Uhlenbecker (1993) collected EUF-I extracted at 200 V and 20 °C for 30 min followed by EUF-II extracted at 400 V and 80 °C for another 30 min in the case of K (Fig. 8.8). Each extraction period was 5 min. In the case of P, Nair and Mengel (1984) considered all the three fractions as a measure of P intensity, while in the case of K, the first two fractions (5–10 min) were considered a measure of K intensity (Sparks, 1987). Since the stepwise extractions will provide an assessment of the changes in the mobility of the nutrient, the slopes of the desorption curves will indicate the rate at which the available quantity of the nutrient will be exhausted. For K, the ratio of the seventh and second fraction has been taken as a measure of K buffer power of the soil in question (Sparks, 1987). Nair and Mengel (1984) and Nair (1992a,b) correlated the EUF fractions with CAL-extractable

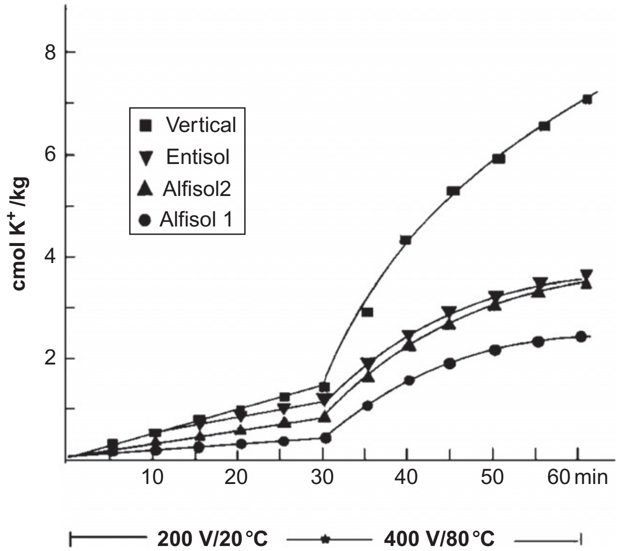

Figure 8.8 Cumulative K^+ extracted by electro-ultrafiltration (EUF). Extraction at 200 V, 20 °C, 30 min ($EUF_{0–30}$ fraction); extraction at 400 V, 80 °C, 30 min ($EUF_{30–60}$ fraction). *After Mengel and Uhlenbecker (1993).*

P (Schüller, 1969) and desorbable P (Nair, 1992a,b), respectively, and the *b* values in the regression functions were used as a measure of P buffer power. The very high *r* values obtained in both of the cases discussed earlier indicate that these *b* values will indeed provide a very dependable measure of P replenishment rates in the rooting zone which the P buffer power, in fact, attempts to measure. While EUF can provide dependable information on both intensity and quantity factors of P and K (Simrad and Tran, 1993; Simrad et al., 1991), it must be pointed out that this facility may not be universally available and is, of course, quite expensive to provide. Thus, in routine soil testing procedures, there is a need to examine alternative procedures to estimate the P and K intensity factors. Nair (unpublished data) has used extractions with 0.1 M $CaCl_2$ in tropical African and Asian soils to quantity P and K intensity. Thus, it is relevant to mention that wherever an EUF facility exists, it could be used to quantify the quantity and intensity factors, and where it is not available, alternate procedures such as extraction with 0.1 M $CaCl_2$ can be used to measure K and P intensity factors. But in both cases, the essential point is that quantifying the P and K buffer power of soils and integrating the buffer power into the computations would provide a much better picture of the soil availability of these nutrients than contemporary soil tests alone.

Additionally, EUF has the possibility to simultaneously provide information on quantity and intensity factors of other plant nutrients, besides P and K, at the same extraction cycles, as for Zn (Nair, 1984a,b).

In a recent study (Steffens, 1994), EUF has been used to study P kinetics. He quantified P kinetics by the Elovich *b* values [similar to that used by Mengel and Uhlenbecker (1993) in the case of K] by stepwise extraction using EUF. In all, 11 fractions were used to study the P kinetics. The first two fractions were obtained, respectively, at 20 °C, 200 V, and <15 mA during an extraction period of 30 min and subsequently at 80 °C, 400 V, and <150 mA during an extraction period of 5 min, that is, a total of 30–35 min. This procedure was similar to that adopted by Nair and Mengel (1984) and Nair (1992a,b). After these two fractions were extracted, nine other fractions were extracted at 5-min intervals at 80 °C, 400 V, and <150 mA. The Elovich *b* values were computed using mg P/kg soil extracted versus time. P uptake was studied during a 4-year period using soils which were treated with basic slag phosphate, super phosphate, partially acidulated phosphate rock, and phosphate rock (Fig. 8.9). The test crops which were successively grown were rye grass

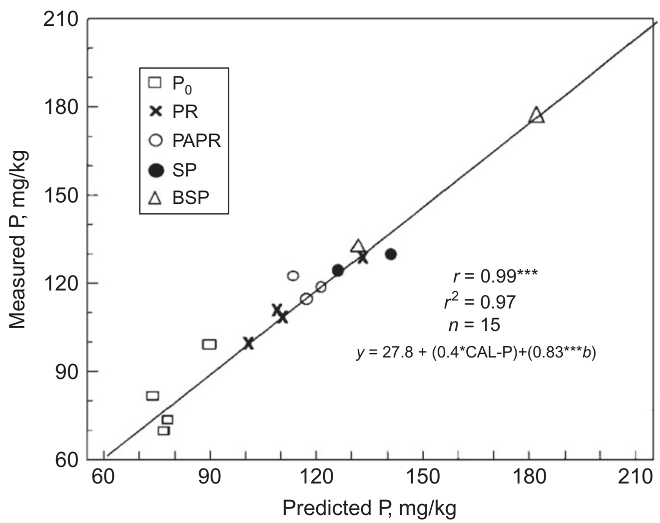

Figure 8.9 Relationship of measured and predicted plant P uptake from pot experiments during a 4-year period (where CAL-P denotes the amount of calcium acetate–calcium lactate–acetic acid–extractable P, and *b* denotes the slope term of the electro-ultrafiltration extraction curves as described by the Elovich equation). P_0, without P fertilization (control); PR, phosphate rock; PAPR, partially acidulated phosphate rock; BSP, basic slag phosphate; SP, superphosphate. *,***Significant at the 0.05 and 0.001 probability levels, respectively. *After Steffens (1994).*

(*L. perenne* L., cv. Taptoe) in the first year, rape (*Brassica napus* L., cv. Akella) in the second year, corn (cv. Badischer Landmais) and summer wheat (*T. aestivum* L., cv. Selpek) in the third year, and summer rye (*S. cereale* L., cv. Sorom) in the fourth year. The Elovich *b* values were more closely correlated to cumulative plant P uptake than water soluble P (van der Paauw, 1971), CAL-calcium acetate + calcium lactate + acetic acid mixture extractable P (Schüller, 1969), or Mehlich 3 extractable P (Mehlich, 1984). The cumulative plant P uptake from the 15 test soils was very well predicted ($r=0.99$) when the Elovich *b* values were also integrated into the multiple regression model $y=a+bx+cz$ used earlier by Nair and Mengel (1984) and Nair (1992a,b), where y denotes the plant P uptake, x denotes the CAL-P, and z denotes the Elovich *b* value. This indicates that considering the Elovich *b* value as a parameter for P release and the quantity of CAL-extractable P for determining P availability following different P fertilizer applications provides a much more reliable estimation of plant P uptake than consideration of only a single parameter of P availability such as the water extractable P, CAL-P, or Mehlich P. The Elovich *b* values used in this investigation are analogous to the P buffer power values of Nair and Mengel (1984) for P, who, for the first time, showed that precise prediction of P availability can only be done when both the labile P and the P intensity are integrated within one framework. Larsen (1967) had postulated such a view much earlier, but experimental evidence utilizing the EUF facilities to measure P intensity as shown by the work of Nair and Mengel (1984) and Nair (1992a,b) for P and by Nair (1984a,b) for Zn came much later. All of these studies underscore the great importance of EUF in modern-day soil testing methods.

6. QUANTIFYING THE BUFFER POWER FOR PRECISE AVAILABILITY PREDICTION—HEAVY METALS

6.1 Zinc

Since Zn, among the heavy metals, has become the most problematic on a global scale, the scope of this review is confined to this very important plant nutrient. There is a great paucity of published material on the effect of buffer power on availability of heavy metals.

Plants obtain most of their fertilizer Zn from reaction products and not applied sources as such, implying that any source of Zn added to soil has to necessarily conform to a chain reaction involving adsorptive, desorptive, and resorptive processes that govern the maintenance of an equilibrium between adequate Zn concentration in the soil solution nearest to the zone of Zn depletion on the one hand and plant uptake on the other. The Zn buffer

power defines this. As Zn concentration in soil solution is normally very low, the supply to plant roots by mass flow can only account for a very small fraction of plant demand. For instance, with a transpiration coefficient of 300 l/kg dry matter and a corresponding Zn concentration of 10^{-7} M in the soil solution, approximately 2 mg of Zn can be supplied by mass flow against a demand of 10–30 mg Zn/kg dry weight of plant tissue. In calcareous soils, as the Zn concentration is of a much lower order of approximately 10^{-8} M, the supply by mass flow could be very much lower (Marschner, 1994) indicating that mass flow can only contribute very negligibly to meet plant needs of Zn. Hence, Zn movement to the plant root surface is principally by diffusion and is essentially confined to a zone around the plant root which hardly extends beyond the root hair cylinder (Marschner, 1994).

Though published papers on the relevance of Zn buffer power in soils to Zn availability are very limited, there is no dearth on other aspects. Genotypic differences to Zn nutrition in a very important crop such as maize, with regard to its hybrids, inbreds, and composites, were reported almost two decades ago in India (Nair and Prabhat, 1977); this study focused on the importance of genetic engineering for tailoring maize varieties for better efficiency of Zn utilization, while the complicated mechanism of Zn–P–Fe interaction was researched even prior to this (Nair and Babu, 1975). In a recent review on the mechanism of Zn uptake, Marschner (1994) indicated that flow culture experiments with various species showed adequate ranges of Zn concentration in the range of 6×10^{-8} to 8×10^{-6} M which are concentrations greater than those that would be expected in the soil solution of most soils. He further pointed out that although work using chelate-buffered solutions has indicated adequate Zn concentrations between 10^{-10} and 10^{-11} M, extremely low adequate Zn concentrations required a concomitant excess of about 100 μM Zn-chelate as buffer at the plasma membrane of the root cells. This implies a need for an unlimited Zn pool for replenishment of Zn^{2+} at the plasma membrane. When plants grow in soil, it is impossible to expect a Zn buffer of this size to exist, and free Zn^{2+} and chelated-Zn concentrations will be at least threefold lower. Hence, critical deficiency or sufficiency concentrations obtained through research employing chelate-buffered solutions cannot be applied to soil-grown plants.

Most of the work on Zn availability to plants in soil is based on chemical extractions among, which DTPA is the most frequently used. The DTPA extraction quantifies a labile fraction of soil Zn comprising water soluble, exchangeable, adsorbed, chelated, and some occluded Zn. The critical

soil level of DTPA extractable Zn can vary from 0.3 to 1.4 mg/kg soil which equates to about 900–4200 g/ha of Zn in heavy soils and about 600–2800 g/ha Zn in light soils in the plow layer (0–20 cm). The crop requirements, on the other hand, are quite small, in the range of 100–300 g/ha for a total dry matter production of about 10 t/ha (Marschner, 1994). The inadequacy of DTPA extraction to reflect plant Zn demand shows that other important factors, such as replenishment of soil solution Zn (Nair, 1984a,b), mobility, and transport to the root surface (Nair et al., 1984; Wilkinson et al., 1968), and also the activity of the roots themselves (Marschner, 1994; Wilkinson et al., 1968), are involved. Since the Zn buffer power is intricately involved in all three factors, the focus of this review is mainly on that attribute.

As early as three decades ago it was suggested that colloidal Zn was released by some specific process associated with root activity (Wilkinson et al., 1968). Conditions in the rhizosphere and particularly root-induced changes markedly affect Zn availability. A difference in rhizosphere pH of as much as 2, higher or lower compared to bulk soil, can be expected to occur as a result of imbalance in ionic uptake. For instance, any acidifying fertilizer such $(NH_4)_2SO_4$ can result in a net excretion of H^+ ions and others such as NH_4NO_3 can result in a net excretion of HCO_3^- or OH^- ions. Additionally, secretion of organic acids and enhanced CO_2 production, as well, will affect rhizosphere pH, and all of the above-mentioned changes will markedly affect Zn availability. However, the scope of this review is confined to the kinetic/dynamic aspects of the changes occurring in the rooting zone mirrored in the Zn buffer power rather than changes in soil reaction in the rhizosphere *per se* on Zn availability.

The distribution of Zn between the solid and solution phases can be described by the buffer power. The availability of soil Zn to the plant depends on the initial Zn concentration, Zn buffer power and effective diffusion coefficient (Barber, 1984). The Langmuir equation gives the relation between B and C_1 as

$$\frac{C_1}{(x/m)} = \frac{1}{aB} + \frac{C_1}{B}$$

where C_1 is the Zn concentration in the soil solution, x/m is the amount of Zn adsorbed per unit of soil, B is the adsorption maximum, and a is a constant related to the soil's bonding energy for Zn. A straight line is obtained when $C_1/(x/m)$ is plotted against C_1 with a slope of $1/B$ and intercept of $1/aB$. The inverse of $C_1/(x/m) = b$, the Zn buffer power, where C_1 and x/m are

both expressed in volume units (Barber, 1984). Using this approach, Shuman (1975) estimated the buffer power values varying from 5 to 100 for four soils representing different major physiographic regions of Georgia. Based on the diffusion model of Drew et al. (1969), Nair (1984a,b) has argued that the $\bar{c}$ in the equation $U = 2\pi\alpha a\bar{c}t$ (Drew et al., 1969), where U is the quantity of Zn absorbed per centimeter root length, a is the root radius in cm, α is the root absorbing power, c is the average Zn concentration on the root surface, and t is the duration of the absorption period, in fact represents an indirect measure of the Zn buffer power. As we already know, the bulk of Zn uptake is by diffusion (Barber, 1984; Elgawhary et al., 1970; Wilkinson et al., 1968). This diffusive process will maintain a concentration gradient in the rooting zone. This concentration gradient will directly affect Zn uptake because of its effect on the average Zn concentration on the root surface. The Zn buffer power will affect this concentration gradient, because the rate of Zn depletion and/or replenishment is mirrored by it. In a sense, the effective diffusion coefficient and the buffer power are analogous for nutrients which are principally absorbed by the plant root through diffusive processes (Nair, 1989). Hence, the crucial question to examine would be the role of Zn buffer power in influencing Zn availability for plant uptake.

6.2 Quantifying Zn buffer power

Nair (1984a,b) used a novel method to quantify Zn buffer power. Nair (1990) has demonstrated the importance of Zn and P buffer power in affecting their bio availability to growing plants. Heavy metal pollution is a major environmental hazard in Europe, especially on the highways due to automobile exhausts; as a consequence, a number of soils are very highly contaminated. Such soils are unsuitable for a precise study on the impact of Zn buffer power on plant Zn uptake, and the choice of soil was narrowed to a heavy clay in the northern part of Belgium containing 1.1 ppm total Zn, 5.5 ppm DTPA extractable Zn, and 0.13 ppm electro-ultrafilterable Zn. The soil was acidic (pH 6.6, 1 N KCl), low in organic carbon (1.8%), high in $CaCO_3$ (16.5%), containing beidellite as the predominant clay mineral. Zn buffer power was quantified by regressing DTPA extractable Zn (y) on electro-ultrafilterable Zn (x) by a stepwise extraction of incubated soil, and the b value in the regression function represented the Zn buffer power. EUF has been employed for a rapid estimation of the intensity of a range of heavy metals, especially in central, western, and eastern European soils (Nemeth, 1979; Nemeth and Recke, 1982). However,

Table 8.7 Correlation coefficients (*r*) between Zn intensity and maize top Zn concentration and total Zn uptake by plant top at harvest without (A) and with (B) Zn buffer power integration

	Correlation coefficient	
Details	**A**	**B**
Zn intensity versus maize top Zn concentration	0.290	0.812*
Zn intensity versus total Zn uptake by maize top	0.356	0.618**

After Nair (1984a,b).
*Significant at 0.1% confidence level.
**Significant at 1% confidence level.

earlier investigations of these authors did not give satisfactory results: analysis of only the alkaline cathode filtrate is insufficient to give precise information about availability indices, primarily due to the fact that the heavy metals are collected by the cathode filter as hydroxides and hydrated oxides, which are hardly soluble in the alkaline cathode filtrate. However, as these oxides comprise soluble and desorbable ions of the heavy metal in question, they are of importance to plant nutrition; Nair (1984a,b) used a modified procedure to bring the oxides into an acid medium for subsequent analysis. The studies indicated that Zn intensity alone is insufficient to precisely predict Zn uptake by maize used as a test plant in the investigation. The relevant data are given in Table 8.7.

Data in Table 8.7 show that the precision of predicting Zn concentration in the maize top increased remarkably, as substantiated by the increase in the coefficient of determination which works out to 65.9%. With regard to total Zn uptake by the maize plant, the increase is less marked, yet substantial. The data show that the major factor responsible for the variance in Zn concentration in the maize top and total Zn uptake by the maize top is the Zn buffer power, and not Zn intensity as quantified by EUF. In a separate experimental setup, Nair et al. (1984) monitored Zn transport by simulation experiments in a laboratory setup using the same field soil and obtained proof to support the hypothesis that it is essentially the buffered Zn that contributes to the major uptake process by the test plant. Dissolved salts in a field soil must move with the liquid, the net movement from a given reference plane being dependent on the activity gradient of salt and water. This naturally brings us to the important question of solute movement within the soil matrix which is dependent on the soil conductivity. Buffered Zn would be in the bulk soil solution to be further transported to plant roots. This transport, though dependent on the soil conductivity, would also be linked to the quantum of Zn *per se* in the bulk

soil solution, which, in turn, would be dependent on the Zn buffer power of the soil in question. Nair et al. (1984) quantified these relationships. In a field soil, it is the buffered Zn which maintains a concentration gradient between the bulk soil solution and the root surface sufficiently conducive for optimal plant uptake. The investigation also showed the ineffectiveness of DTPA extraction as a reliable soil test for Zn availability. EUF is being put to use increasingly for commercial soil testing in many countries in Europe, notably, for sugar beet cultivation in Austria. Determination of Zn intensity singly may not provide reliable information regarding plant available Zn. Besides Zn intensity and Zn buffer power, other soil factors have only a minor influence on Zn absorption. EUF has the advantage of a rapid assessment of the Zn intensity factor. Combining the advantage of rapid assessment of the intensity factor of the nutrient with its corresponding buffer power might greatly enhance the reliability of fertilizer recommendations not only for Zn, but, perhaps, for other heavy metals as well, making EUF a reliable tool in soil testing for heavy metals.

CASE STUDIES WITH ASIAN SOILS

6.3 South Asian soils

The just concluded (October 2011) 3rd International Zinc Symposium in Hyderabad, India, in which 195 delegates from 30 countries participated, focused on the cruciality of Zn in both plant and human nutrition. Zn is assuming the role of a major constraint in crop production. There is widespread Zn deficiency in topical soils. This section of the review is divided into two parts, where the focus will be first on (A) South Asian soils, India being the classical example and (B) Central Asian soils, Turkey, where severe Zn deficiency in the main wheat growing belt of the country (Anatolia) is threatening wheat production and adversely affecting human nutrition.

Investigations in Indian soils. The lateritic belt of Kerala State, in southern India, was chosen as the test soil. The economic mainstay of the State is black pepper (*Piper nigrum* L.). The crop is very susceptible to Zn deficiency and among the major diseases causing havoc in black pepper plantations, the onset of the "Quick Wilt" caused by *Phytophthora* spp. (*Phytophthora capsici*) has been attributed to a severe Zn deficiency in the soil. The "official" recommendation for supplemental Zn fertilizer is based on the classical DTPA extraction,

and a "blanket" recommendation for the entire State is made, where the farmers are advised to apply Zn fertilizer at the rate of 25 kg/ha for the entire State. This author has, for long, suspected the advisability of making such a "blanket" recommendation, and had suggested, in its place, investigating the Zn buffering mechanism of the soils and then calibrating Zn fertilizer recommendations based on this. Zn fertilizer is quite expensive, and, at the prevalent rate of approximately Rs. 300/kg (approximately U.S. $/kg) could turn out to be prohibitively expensive for a poor black pepper farmer. In the following paragraphs, the salient results are summarized.

6.3.1 Quantifying the Z buffer power of the pepper-growing soils

Nair (1984a) has used EUF to quantify Zn "intensity" in measuring Zn buffer power of European soils. Because the procedure is very highly sophisticated, and due to the non availability of such expensive instruments in a country like India, and many other developing countries, a simple adsorption–desorption equilibrium technique was developed by the author (Nair, 2002) to quantify Zn buffer power of black pepper-growing soils. For this, 200 g of representative soil samples from the principal black pepper-growing regions were selected from the State, incubated at 60% of the maximum water holding—capacity with graded rates of Zn, over a fortnight, by maintaining the water regime to constancy. At the end of the period, the soil samples were extracted with 0.01 M $CaCl_2$ over a 24-h period and the extract tested for Zn using atomic absorption spectrophotometry. This represented Zn "intensity." Separate extractions were made with DTPA, which represented the Zn "quantity." Data in Table 8.8 indicate that the Zn buffer power values of the black pepper-growing soils varied widely (Photo 8.3).

Table 8.8 Zinc buffer power of black-pepper-growing soils

Soil	"*r*" Value	"*b*" Value
Peruvannamuzhi	0.8337***	0.7824
Thamarasseri	0.9304***	1.5786
Ambalavayal	0.9604***	3.0358

Notes: All the "*r*" values are very highly significant, at a confidence level of 99.9% (***) implying that the adsorption–desorption equilibrium technique developed by the author provides an accurate measure of the Zn buffer power. Further, the soils showed widely varying Zn buffer power, as shown by the "*b*" values, with the soils from *Peruvannamuzhi* region least buffered for Zn, while that from the *Ambalavayal* region most buffered, with the soils from *Thamarasseri* region intermediate in their Zn buffer power. These findings have remarkable impact, as we shall see from the results incorporated in Table 8.10.

Photo 8.3 Effect of Zn fertilizer application on Bush pepper based on the soil's Zn buffer power in Kerala State, India.

Data in Table 8.8 bring to light two very important facts. First, the very highly significant correlation coefficients ("*r*" values) prove that the technique employed allows a precise determination of the Zn buffer power of the soils investigated. Second, the soils varied widely in their Zn buffer power. It is this fact which has to be critically viewed against the existing Zn fertilizer recommendation, emanating from routine soil tests using the universally employed DTPA extraction, to understand the cruciality of the Zn buffer power for precise formulations of Zn fertilizer application for black pepper.

Data in Table 8.9 clearly indicate that integrating Zn buffer power has improved the interrelationship between DTPA routine soil test versus both Zn concentration in plant top and Zn uptake. Most remarkably, the overall relationship between DTPA soil test and dry matter production not only improved very significantly when Zn buffer power was integrated into the computations, but from a negative value to a positive one. This implies two very important conclusions. First, the universally adopted DTPA soil test for Zn is unsuitable for the soils investigated. Second, it is the Zn buffer power that is the decisive factor which determines dry matter production, implying, higher the Zn buffer power, more the yield. Results in Table 8.10 substantiate this very important conclusion.

Data in Tables 8.7, 8.11, and 8.10 have to be reviewed in conjunction to precisely understand the cruciality of the "Buffer Power Concept." Black pepper is the economic mainstay of the Kerala State. Of late, widespread Zn deficiency has been observed in the State, and the onset of the most

Table 8.9 Linear regression functions ($Y = a + bx$) and correlation coefficients ("r" values) for the relationship between DTPA extractable Zn (Zn "quantity" Y) and 0.01 M $CaCl_2$ extractable Zn (Zn "intensity" x)
Regression function

Soil	Adsorption–desorption equilibrium	Soil incubation	"r" Value	
			A	B
Konya (Central Anatolia)	$Q = 201bI + 5.3$	$Q = 679bI - 5.9$	0.951*	0.978*
Koruklu (Gap region)	$Q = 17bI + 17.9$	$Q = 375bI - 8.7$	0.015	0.784*
German soil (reference soil)	$Q = 8bI + 6.5$	$Q = 11bI + 7.8$	0.972*	0.942*

Notes: Q = Zn "quantity," I = Zn "intensity," b = Zn buffer power. A without the integration of Zn buffer power ("b" values) in the computations, B with the integration. The experimental technique employed has resulted in very highly significant correlation coefficients ("r" values), except in the case of soils from the Gap region (Koruklu) in the case of the incubation experiments, which suggest the high accuracy of the adsorption–desorption equilibrium technique to determine Zn intensity, which is a true reflection of the Zn buffer. Note the remarkable improvements in the "r" values (B compared to A) which unequivocally show that the integration of the Zn buffer power remarkably improves the relationship. How this affects plant uptake, and, eventually wheat yields, will be discussed in the following tables and explanation of experimental details.
*Significant at a confidence level of 99.9%.

Table 8.10 Black pepper yields from farmers' fields weighted against the Zn buffer power

Region	Yield (kg/vine)		Deviation (%)
	Targeted	Actual	
Peruvannamuzhi	0.241	0.401	+66
Thamarasseri	0.490	0.487	+0.6

Notes: Target weighting was done against the highest vine yield obtained from the *Ambalavayal* region. Note the remarkable closeness between targeted and actual yields in *Thamarasseri* region, whereas in *Peruvannamuzhi* region, there is a huge deviation. Soils in the *Peruvannamuzhi* region are atypical black pepper soils. Ironically the "official" recommendation for Zn fertilizer recommendation emanate from experiments conducted in *Peruvannamuzhi*, as the black pepper research station, affiliated to the Indian Institute of Spices Research in Calicut, Kerala State, is situated here.

devastating "Quick Wilt" disease and "Foot Rot" disease, both of which can exterminate a black pepper plantation in a matter of a week's time, has been attributed to the infestation by *Phytophthora* fungi, which thrives best in Zn-deficient soils. The scientists at the Indian Institute of Spices Research in Calicut, Kerala State, India, under the administrative control of the Indian Council of Agricultural Research in New Delhi, have made a "blanket"

Table 8.11 Correlation coefficients ("*r*" values) for the interrelationship between routine DTPA soil test versus Zn concentration, Zn uptake and dry matter production without (1) and with (2) Zn buffer power integration in black pepper

Details	1	2
Zn concentration versus DTPA test	0.88*	0.92*
Zn uptake versus DTPA test	0.78	0.86*
Dry matter production versus DTPA test	−0.74	0.78*

*Significant at 99.9% confidence level.

recommendation of soil application of 23 kg $ZnSO_4$/ha, when DTPA extractable Zn is less than 1.6 ppm. In terms of monetary input, this would translate to more than U.S. $ 25/ha in terms of farmer investment. Because the soils are variously Zn buffered (Table 8.8), a single "blanket" dose as the Kerala Government is propagating is totally unscientific, because, where the farmer needs to apply only lesser quantities of Zn, he would end up applying more and thus waste his money, if he were to go by the routine DTPA soil test values. To elaborate, the soils from the *Ambalavayal* region have a Zn buffer power of 3.0358 as compared soils from the *Peruvannamuzhi* region which have a buffer power of only 0.7824. In other words, the *Amabalavayal* soils have the potential, which is early more than fourfold, to supply Zn as compared to *Peruvannamuzhi* soils. In practical terms, this would imply that the *Ambalavayal* soils would only require 25% of the total quantum of Zn applied to *Pervannamuzhi* soils. Translated into the recommendation, it would imply that the *Ambalavayal* soils would only need about 5 kg Zn fertilizer/ha when the *Peruvannamuzhi* soils require 23 kg/ha. In the case of *Thamarasseri* soils, the quantity required would be approximately 50% of the recommended rate. The pecuniary benefits to the poor black pepper farmer can easily be gauged from this sound and practical reasoning (Photos 8.4 and 8.5).

In fact, the scientists at the Indian Institute of Spices Research have made a gross underestimation of the Zn-supplying power of the soils in the State, because, their results and recommendations are all based on the soils of the *Peruvannamuzhi* region, where the black pepper research station is located. The soils here are acutely Zn impoverished, but, that is not the case in the entire State of Kerala. This also shows that, more often than not, practical recommendations from experiment stations, when extrapolated on a large-scale, can run into real problems, especially when such recommendations are based on routine soil testing procedures and the poor farmers could

Photo 8.4 Black pepper in farmers' fields, Kerala State, India.

Photo 8.5 Black pepper plantation in Kerala State, India.

be at the receiving end of losing money. These results (Nair, 2004) substantiate the earlier ones (Nair, 2002) on the importance of precisely quantifying the Zn buffer power, rather than routinely estimate DTPA extractable Zn. This approach is further discussed in the case of the author's investigations in Turkey (Central Anatolia), where severe deficiency is causing great adverse effects on what production. Farmers have been advised to apply as much as 100 kg $ZnSO_4$/ha, as a blanket recommendation, without obtaining any tangible and consistent response in wheat yield. Hence, the great economic importance of the "Buffer Power Concept," as against routine soil testing

Photo 8.6 Shoot borer infestation in cardamom.

procedures, needs hardly any underscoring. Nair et al. (1997) have conclusively demonstrated the importance of the Buffer Power Concept in the case of potassium nutrition of cardamom (Elettaria cardamom M.), another very important spice crop, besides black pepper, in the State of Kerala (Photo 8.6).

6.4 Central Asian soils

In a global study initiated by FAO and carried out in 30 countries, it was estimated that about 30% of the agricultural soils of the world are Zn-deficient (Sillanpaa, 1982). Based on the analysis of 298 soil samples, Turkish soils were classified as Zn-deficient (Sillanpaa and Vlek, 1985). Acute Zn deficiency triggering severe decreases in cereals yields have been noted in many countries of the tropical belt. Cereal species show large differential sensitivity to Zn deficiency. Large differences in sensitivity to Zn deficiency is also seen among genotypes within a specific cereal species

(Graham and Rengel, 1993). This indicates the existence of genetic potential to select and breed for Zn deficiency resistant genotypes. Among the cereals, wheat is particularly sensitive to Zn deficiency. Growing wheat on Zn-deficient soils leads to not only decrease in plant growth and yield, but would also lead to low Zn accumulation in grains. This will have a deleterious effect on human nutrition, because wheat grains are rich in phytate and fiber, which limit absorption and/or utilization of Zn in human cells (Welch, 1993). Approximately 40% of the world's population suffer from micronutrients, including Zn, deficiency (Graham and Welch, 1994). High consumption of cereal-based foods is thought to be one of the major reasons for Zn deficiency in humans. The proportion of wheat, maize, and rice consumed in diets of people in developing countries comprises about 90% of the average diet (Graham and Welch, 1994). In Turkey, in Central Asia, it has been observed that Zn deficiency in humans is widespread where cereal-based foods dominate (Cavdar et al., 1983; Prasad, 1982). Turkey is one of the major wheat producing countries in the world. Nearly 45% (4.5 million ha) of the wheat producing area in Turkey is located in the highly calcareous region of Central Anatolia. Central Anatolia is semi arid, being the driest region of Turkey. Scanty rainfall (about 325 mm) and low water supply greatly limit wheat yields. The author initiated a project to critically examine the role of the Buffer Power Concept in the Zn nutrition of wheat, as inconsistent results have been observed even with huge quantities (as much as 100 kg $ZnSO_4$/ha) of Zn application to the wheat crop.

Very recently, Nair (unpublished data) employed an adsorption–desorption equilibrium and a soil incubation technique to quantify the Zn buffer power of some highly Zn-deficient Turkish soils which have failed to show consistent response to Zn application based on DTPA extraction in wheat grown in these soils. Despite quite comparable DTPA extractable Zn, the Zn buffer power of these soils varied largely from a low value of 27 to a very high value as high as 200. It is being hypothesized that the Zn buffer power could, possibly, hold the key to explaining the differential response of wheat to Zn application in these problematic soils. The technique developed by Nair (unpublished data) dispenses with the need to employ highly cost intensive EUF, which will certainly not be suitable to practical situations in many developing countries constrained by economic considerations, and in its place, employs a far simpler, and, simultaneously, far less costlier, technique of quantifying Zn intensity by an adsorption–desorption equilibrium technique using 0.01 M $CaCl_2$ solution or soil incubation technique.

Establishment of the Zn buffer power. The Zn buffer power curves are represented by the plot between the Zn "quantity" and Zn "intensity" parameters (Nair, 1996). The "*Q*" and "*I*" parameters were established by laboratory procedures, one where an adsorption–desorption equilibrium technique was employed and another where an incubation technique was used, as described below.

Adsorption–desorption equilibrium technique to measure Zn "intensity". 5 g soil were weighed into PVC tubes saturated with 25 ml Zn solution ($ZnSO_4 \cdot 7H_2O$) in 0.01 M $CaCl_2$ solution in amounts ranging from 0 to 500 mg Zn/kg soil. The soil suspensions were shaken in an end-over-end shaker at ambient temperature (±25 °C) at 125 cycles/min. After 24 h the suspensions were filtered through "Blue Ribbon" 589 cube (3)—150-mm filter paper (Schleicher and Schuell—German make). The soil on the filter paper was thoroughly washed with double distilled water and subsequently with 60% ethanol to remove any Zn ions not bound to the soil matrix and the entire mass of soil was transferred to another set of PVC containers. The filtrate was immediately analyzed for Zn using atomic absorption spectrophotometry.

Estimation of Zn "intensity". To the new set of PVC containers with the soil mass, 25 ml of 0.01 M $CaCl_2$ solution were added and they were shaken for 24 h under identical conditions, as explained above. After 24 h, the suspensions were filtered, as before, and the filtrate immediately analyzed for Zn. This represents Zn "intensity."

Estimation of Zn "quantity". The soil in the PVC containers was extracted with DTPA extractant, which is a mixture of 0.005 M DTPA, 0.01 M $CaCl_2$, and 0.1 M TEA, adjusted to a pH of 7.3 using 6 N HCl. The pH of the extractant was monitored using a portable pH meter. Twenty-five milliliters of the extractant was pipetted into the PVC containers and the soil suspensions were shaken as before, but, only for 2 h. The extraction period is crucial as originally suggested by the authors, since extraction is not complete after 2 h, the labile and nonlabile quantities of Zn continuing to dissolve. The filtrate was immediately analyzed for Zn by atomic absorption spectrophotometry and the Zn concentration in the filtrate was expressed as mg Zn/kg soil (ppm).

Each of the soil series had six Zn treatments, including a "No Zn" control treatment, and each treatment was replicated thrice to conform to a Completely Randomized Block Design. Thus, in all, in each cycle of operation, there were 54 samples and each was analyzed, at every stage, in duplicate.

The most important conclusions of great practical significance, emanating from these investigations, are the following. First, there is a very high correlation coefficient (0.8660^{***}, significant at 0.1% confidence level) between Zn buffer power and percentage increase in wheat grain yield (Table 8.12). This unequivocally establishes that the single most important determinant in wheat yield increase is the soil's Zn buffer power. Both the experimental soils from Turkey were critically Zn-deficient (<1 mg Zn/kg soil, i.e., 1 ppm), while the German soil had 3.6 mg Zn/kg soil (3.6 ppm). And a uniform rate of 100 kg $ZnSO_4$/ha as $ZnSO_4 \cdot 7H_2O$, was applied to both soils. Yet, there was a huge margin of difference in the mean wheat grain yield (Table 8.13). The percentage increase in mean wheat grain yield in Konya soils, which are very highly Zn buffered, is 69 while those from Kuruklu, where the Zn power had a very low value, showed but negligent increase in wheat yield. The percentage increase coefficient of determination for the interrelationship between Zn buffer power and mean increase in wheat grain yield is 74. This simply illustrates that nearly 75% of yield variation can be explained by the Zn buffer power. The soil Zn dynamics which explains this phenomenon is as follows.

That Zn is principally transported through the diffusive mechanism is now an established fact and Nair (1984a,b) has provided experimental evidence where Zn buffer power is shown to be the most important criterion affecting the uptake process. Flux rates thus depend on Zn concentration gradients between root surfaces and the bulk soil solution (Nair et al., 1992). Current results have to be viewed against this background. According to the model of Zn uptake proposed by Nair (1984a,b), the average concentration on the root surface is analogous to Zn "intensity" parameter, and so would critically affect the Zn uptake process. A root growing into the soil would, at first, encounter a relatively high Zn concentration at its surface,

Table 8.12 Interrelationship between Zn availability parameters and wheat grain yield and shoot tissue concentration of Zn (Turkey)

Parameter investigated	Correlation coefficient ("*r*" value)
DTPA soil test Zn versus Zn concentration in shoot tissue	0.672^{***}
Zn buffer power versus percentage increase in wheat grain yield	0.860^{***}

Notes: Note the very highly significant (at a confidence level of 99.9% (***)) "*r*" value between Zn buffer and percentage increase in wheat grain yield. Though DTPA soil test seems to have a positive influence on shoot Zn concentration, it is the Zn buffer power that yields far greater influence on wheat grain yield.

Table 8.13 Effect of Zn fertilization (100 kg $ZnSO_4$/ha) on mean and range of Zn shoot tissue concentration and grain yield among 28 wheat genotypes grown in Konya soils and 25 grown in Gap soils in Turkey

Soil	Tissue concentration (ppm)				Grain yield (kg/ha)				Percentage increase
	Without Zn		With Zn		Without Zn		With Zn		
	Range	Mean	Range	Mean	Range	Mean	Range	Mean	
Konya	7–10	9	10–19	14	1550–4010	2710	248–5900	4570	69
Gap	16–23	19	22–31	25	1530–5260	3500	1550–5300	3510	0

Notes: The Zn buffer power is very clearly reflected in grain yield increase. Note that the "*b*" values (Zn buffer power) for both the adsorption–desorption equilibrium technique and incubation technique for Konya soils are 201 and 679, respectively. The corresponding values in Koruklu soils (Gap region) are 17 and 375, respectively. The percentage increase in wheat grain yield in Konya soils is 69 while that in Koruklu soils 0. In other words, the Konya soils are highly buffered for Zn availability.

which would be more or less equal to the Zn concentration in the bulk soil solution. Due to root uptake of Zn, its concentration on the root surface would diminish. This decrease would not only depend on the uptake rate, but, also on the Zn buffer power, because, the Zn buffering mechanism would govern the rate of replenishment in the zone of Zn depletion around the roots. A soil with a high Zn buffer power would replenish the depleted soil much faster than a soil with low Zn buffer power. This differential mechanism is reflected in the Zn buffer power values (Table 8.9) of the soils from Konya and Kuruklu. Thus, it is logical to conclude that the uptake model proposed by Nair (1984a,b) clearly explains the yield differential in the two soils investigated. The Konya soils, by virtue of their very high Zn buffer power, are able to maintain optimal Zn concentration on the wheat root surface and this positive impact is reflected in grain yield increase. The Kuruklu soils are unable to maintain the optimal Zn concentration on root surface, hence are unable to sustain high wheat yields (Table 8.13).

CASE STUDIES WITH AFRICAN SOILS

Central African soils—the Republic of Cameroon. The Republic of Cameroon is a small country in Central Africa. Soils are lateritic, highly acidic, and soil pH ranges between 4.5 and 5.0. The country's agricultural scenario is confined mainly to cocoa, coffee, and rubber. Among the cereals, both rice and maize are popular. The country has a huge animal population, and good, and nutritious fodder is a great necessity of the country. With this view in background, an attempt was made to introduce white clover (*Trifolium repens* L.) from the United States, and the following investigations refer to the role of "The Nutrient Buffer Power Concept" in the nutrition of white clover.

Experimental soils. The soils investigated are widely varying. Their physicochemical properties are listed in Table 8.14.

The main objective of this investigation was to examine how well "Buffer Power Concept" explains soil availability of P and K in very problematic African soils. And, white clover was chosen as the test crop because there is acute shortage of palatable and nutritious fodder for the livestock in the country. What is generally fed to the cattle is the post harvest waste of either rice or maize. This does not ensure good milk yield. It was thought that livestock industry had a tremendous potential in the country and white clover was chosen as the test crop. The seeds were obtained through a

Table 8.14 Physicochemical properties of the experimental soils

Details	Soil 1	Soil 2
Sand (%)	48	7
Silt (%)	18	41
Clay (%)	34	52
Organic carbon (%)	5.6	8.2
Total N (%)	0.37	0.48
pH (1 N KCl)	4.4	5.0
CEC (mequiv./100 g soil)	9.5	20.7
Base saturation (%)	21.8	32.2
Available P (ppm)	2.1[a]	13.0[a]
Available P (ppm)	3.7[b]	4.7[b]
Available P (ppm)	Tr.[c]	3.2[c]
Available K (mequiv./100 g soil)	0.18[d]	0.27[d]
Available K (mequiv./100 g soil)	0.17[c]	0.21[c]

Notes: All of the below-mentioned soil tests are "routine" soil tests for available P and K. The only exception is the 0.01 M $CaCl_2$ extraction which gives the P concentration in the equilibrium suspension of soil (Mattingly et al., 1963).
[a]Olsen's test.
[b]Bray II test.
[c]0.01 M $CaCl_2$ extraction.
[d]NH_4OAc test.

Memorandum of Understanding between The University Center, Dschang, The Republic of Cameroon, and the University of Florida (Institute of Food and Agricultural and Forest Sciences), in Gainesville, Florida. The investigation was confined to two soil types with very divergent physic-chemical characteristics (Table 8.14). Soil 2 is highly fertile compared to Soil 1.

Data in Table 8.15 clearly indicate that the experimental technique devised by this author has resulted in a remarkable positive interrelationship between the Q/I measurements. The very highly significant (at 99.9% confidence level) "r" values substantiates this contention. Also, soil 2 has a much higher P and K buffer power compared to soil 1. What follows is the further examination of the question whether integrating the P and K buffer power into the computations enhances predictability of the P and K concentration in plant top, and, eventually, P and K uptake. Answers to this question are presented in Table 8.16.

Table 8.15 Linear regression functions ($Y = bx + a$) and correlation coefficients ("r" values) for the interrelationship between Olsen's P test (Y = P "quantity") versus 0.01 M $CaCl_2$ extractable P (x = P "intensity"), and NH_4OAc extractable K (Y = K "quantity") versus 0.01 M $CaCl_2$ extractable K (x = K "intensity")

Nutrient	Soil	Regression function	Correlation coefficient ("r")
P	1	$0.41x + 0.24$	0.994*
	2	$0.47x + 2.37$	0.890*
K	1	$0.17x + 0.10$	0.960*
	2	$1.28x + 0.17$	0.940*

Notes: "b" in the regression function refers to the buffer power of the nutrient in question, a = a constant.
*Significant at a confidence level of 99.9%.

Table 8.16 Correlation coefficients for plant top concentration and plant top uptake of P and K without (A) and with (B) the P and K buffer of the experimental soils

Details	A	B
P concentration versus Olsen's soil test	0.61*	0.69*
K concentration versus NH_4OAc soil test	0.05	0.62*
P uptake versus Olsen's soil test	0.17	0.77*
K uptake versus NH_4OAc soil test	0.18	0.78*

*Significant at a confidence level of 99.9%.

Data in Table 8.16 unequivocally establish the important fact that integration of the buffer power, both in the case of P and K, enhances predictability of P concentration in plant top and P uptake, so also K concentration in plant top and K uptake, in a very highly significant (at a confidence level of 99.9%) manner. More than this, there are other very important additional features of the results, which follow. That is, first, inasmuch as the P and K uptake process is concerned, neither of the widely practiced routine soil test for P, that is the Olsen's soil test, nor the NH_4OAc test for K, showed any positive statistically significant relationship. This is reflected in the very low "r" values (Table 8.16). But, most remarkably, these "r" values shoot up to very highly significant ones (at a confidence level of 99.9%) when the corresponding P and K buffer power values are incorporated into the computations. In fact, in the case of Olsen's soil test, for P uptake, the coefficient of determination increases from a mere 2.9% in the absence of the P buffer power to 59.3% when the corresponding P buffer power value is also integrated into the computations. In the case of the routine NH_4OAc extraction

for K uptake, the corresponding values are 3.2% and 60.8%. The coefficient of determination is a precise measure of the accuracy of prediction. In other words, these results unequivocally demonstrate that by integrating the respective P and K buffer power values into the computations, a substantial variance in P and K uptake by plant top can be explained. This is, indeed, a very remarkable observation of this investigation, which has considerable significance in white clover production in Cameroon. This is, because, once the P and K buffer power values of the soils in question are determined, to begin with, the application of the important plant nutrients through their respective carriers (chemical fertilizers) could be appropriately designed. This has very extensive practical consequence in white clover production in Cameroon. Most remarkably, in the case of K, the coefficient of determination for plant top concentration increased from a mere 0.25% to 38.4%. This translates into a 15,360% increase in variance prediction.

Results in Tables 8.17 and 8.18 have an important bearing on the practical aspects of white clover production in Cameroon, vis-à-vis "The Nutrient Buffer Power Concept." The most important conclusion is that among the two nutrients investigated, namely, P and K, response to P fertilizer application has shown a consistent pattern, with both higher dry matter production and P uptake. With enhanced P fertilizer application rates, there has

Table 8.17 Plant top dry matter production (kg/ha) and P uptake (kg/ha) from the experimental soils as a function of P fertilizer application

	Dry matter production (kg/ha)				P uptake (kg/ha)			
	P application rate (kg/ha)				P application rate (kg/ha)			
Soil	**0**	**12.5**	**25**	**37.5**	**0**	**12.5**	**25**	**37.5**
1	29	62	78	76	43	95	152	191
2	67	96	99	93	106	154	176	181

Table 8.18 Plant top dry matter production (kg/ha) and K uptake (kg/ha) from the experimental soils as a function of K fertilizer application

	Dry matter production (kg/ha)				K uptake (kg/ha)			
	K application rate (kg/ha)				K application rate (kg/ha)			
Soil	**0**	**50**	**100**	**200**	**0**	**50**	**100**	**200**
1	32	24	27	20	1371	959	1071	737
2	65	73	76	87	2989	3675	3815	4576

been consistent increase in dry matter production and P uptake. The magnitude of dry matter production and P uptake in response to enhanced P fertilizer application has been more in the case of soil 2 as compared to soil 1. When we come to K fertilizer application and crop response, it has been quite inconsistent. The consistent and better response in soil 2 as compared to soil 1 can be traced to its much better buffer power (Table 8.15).

What are the implications of this finding in white clover production in Cameroon?

The Republic of Cameroon is an emerging and stable country (bilingual—both French and English) on the African continent, with a small population, but, with vast natural resources like oil, minerals (especially bauxite, raw material for aluminum, which is much sought after by aerospace industry), agriculture (specially cocoa production, second highest producer on the African continent next to Ghana), and a vast potential for tourism. It has a stable livestock industry (cattle production) which has a very bright future. Though on the countryside of the natural grazing is the common route for cattle feeding, things are giving way to supplemental fodder feeding. It is here the potential for white clover cultivation emerges. This author imported the seeds of white clover from the United States and the results of the experiments reported here are from the imported seeds. The objective behind this investigation was to popularize the cultivation of white clover in Cameroon and it is seen that the "Buffer Power Concept" has a major role to play in its nutrition, inasmuch as P and K nutrition of the plant is concerned, as could be clearly deduced from the experimental results discussed above.

This research formed part of a Master's thesis of one the author's students, while he held the position of Professor and Head of the Department of Soil Sciences at The University Center, and was selected as the best thesis submitted to the University for the Master's degree and received a sum of 400,000 CFA (equivalent to more than U.S. $1000) awarded in recognition of the academic excellence of the research by the organization for advancement of science on the African continent. The award was given by the Minister of Higher Education and Scientific Research, on behalf of the President Paul Biya, of The Republic of Cameroon, and was celebrated as a very important national event.

6.5 Other heavy metals

One other important aspect to be considered, which is of relatively recent origin, is the heavy metal contamination of agricultural soils and their toxic

effects on buffering. An element of particular interest is cadmium (Cd). The main sources of Cd contamination of agricultural soils are through the application of mine wastes, sewage sludges, and other residues. Kuo (1990) has reported on Cd buffering capacity and accumulation in Swiss chard (*B. vulgaris* L.) in sludge-amended soils. He reported that while DTPA extractable Cd did not show a high correlation with plant Cd, the Cd buffering capacity and plant Cd were very highly correlated.

6.6 Molybdenum

Dissolved soil molybdenum can buffer under a wide range (Barber, 1995). Values ranging from 9 for a sandy loam to 83 for a silty clay loam have been obtained (Lavy and Barber, 1964). If the concentrations of adsorbed molybdenum, which varied from 0.6 to 1350 μg/kg with solution molybdenum concentrations which varied from 1 to 13 μg/l are compared, a buffer power range from 1 to 100 is obtained as indicated by the data of Lavy and Barber (1964). By comparison, Australian soils indicated a buffer power range of 10–2000 (Barrow, 1970). Such very high buffer power values will greatly affect molybdenum uptake by plants growing in these soils. Since both mass flow and diffusion under differing molybdenum concentrations in the soil solution will affect its uptake, the precise quantification of the buffer power assumes greater relevance in predicting molybdenum availability. Since, for a given soil, molybdenum uptake by the plant growing in it will increase as its pH increases, ruminants which consume forage grown on such soils would develop molybdenosis, a disorder related to excessive intake of this element. A prior knowledge of the molybdenum buffer power will help manage better molybdenum fertilization of such soils. Additionally, the excess presence of both phosphate and sulfate will affect molybdenum availability in soils, but, their effect on molybdenum buffer power has to be clearly elucidated. There is, but scant, information on these aspects.

6.7 Iron

The iron buffer power has to be related to both soil adsorbed iron and soil solution iron. Since redox reactions, precipitation, and the presence of iron in organic complexes will affect the equilibrium between adsorbed and soil solution iron, it will be difficult to precisely quantify the iron buffer power of agricultural soils. O'Connor et al. (1971) obtained a buffer power value of 1000 for $^{59}Fe^{2+}$ added to a thoroughfare loamy sand having a pH of 7.9. Since this value increased with time, it might have been affected by

precipitation of iron oxides. Inasmuch as iron uptake from soils is concerned, one crucial factor would be root activity. The secretion of Fe-chelating phytosiderophores by Fe-deficient graminaceous species and further the production of siderophores which are low-molecular-weight iron chelating agents produced by almost all bacteria and fungi under iron limiting conditions (Buyer and Sikora, 1990) would make it difficult to quantify Fe flux by mass flow and diffusion, particularly the latter, on which Fe availability based on its buffer power hinges. The effect of both phytosiderophores and siderophores will assume crucial significance in soils of high pH, wherein, these materials will solubilize iron and allow its movement both by mass flow and diffusion to the root surface. Since the ability of plant root to secrete phytosiderophores is both species and cultivar specific, there is an imminent need to understand better how this phenomenon might possibly affect Fe buffering at the soil–root interface.

6.8 Manganese

The range in Mn buffer power is greater than those for most other nutrients. Investigations on Mn buffer power are scanty. Though Mn buffer power can be calculated from data on exchangeable Mn and soil solution Mn, the validity of such values is questionable because soil solution Mn has two components, namely, ionic and complexed, and their combined presence will render the Mn buffer power calculations invalid. Large variations have been found between exchangeable Mn and soil solution Mn. Barber et al. (1967) reported values ranging from 527 to 1.1 for these two fractions. Halstead et al. (1968) found narrower (65 to 0.4) ratios. Soils with low soluble Mn have been found to have high values while the reverse is true with regard to acid soils where Mn levels are high (Barber, 1995).

6.9 Boron

The buffer power for *B* has been calculated from adsorption curves and values less than 3 have usually been found (Barber, 1995). For a loam soil, values of 1.35 and 1.7 have been found (Sulaiman and Kay, 1972). The absorption of *B* by plant roots would differ from that of other ionized species since *B* is present in solution as undissociated H_3BO_3 (Barber, 1995). Since the buffer power values for *B* are generally small, it implies that the effective diffusion coefficient for *B* will be large and this in turn results in relatively easy long distance transport of *B* by mass flow and diffusion to reach plant

root (Barber, 1995). Obviously, much of the *B* that is diffusible will reach the plant root during the period of plant growth.

7. INFLUENCE OF HEAVY METAL CONTAMINATION ON BUFFERING OF MAJOR ELEMENTS

With the increased use of sewage sludges and other residues in farming, there is a need to understand the effect of heavy metals carried in these materials on buffering of other major nutrients. Though interaction between heavy metals such as Zn and Fe with P has been studied in great detail (Nair and Babu, 1975) there is little information on the effect of heavy metals such as Cd or Cu on the buffering of other major nutrients. Yang and Skogley (1990) have studied the effect of Cu and Cd on K adsorption and K buffering capacity. When Cu or Cd are introduced into the soil as salts (Yang and Skogley, 1989) or when metals accompany sludge applications (Page et al., 1987), soil solution concentration and plant uptake of these metals is extremely low. Consequently, metal adsorption by soil components is important in regulating soil solution metal concentration, bioavailability, and the toxicity that some of the heavy metals may cause in crop production. Since K is found to be highly vulnerable to adsorptive–desorptive (exchange) reactions, the large application of these metals might affect K dynamics. Yang and Skogley (1990) reported that K buffering was reduced by 20–32% by Cu addition and 7–20% by Cd addition. The rate of application was 400 mg Cu or Cd/kg soil. Cu and Cd changed the distribution of K, Ca, and Mg between the soil and solution. These results suggest that Cu or Cd addition would influence soil K availability by changing K adsorption kinetics, buffering capacity, and distribution.

8. POSSIBLE BUFFERING EFFECT ON PLANT ACQUISITION OF HEAVY METALS

There is now growing evidence that root-induced changes are primarily responsible for the differential uptake of heavy metals such as Fe and Zn. In a recent review on Fe nutrition, Marschner and Römheld (1994) reported that two different types of root response strategies to Fe deficiency are identified in all plant species. In strategy I, occurring in all plant species except grasses, a plasma membrane-bound reductase is induced with enhanced net excretion of protons. In strategy II, confined to grasses, there is an increase in the biosynthesis and secretion of phytosiderophores which

form chelates with Fe^{3+}. Compared to the progress made in identifying the cellular mechanisms of root responses in strategy I and strategy II plants, the understanding of processes taking place in the apoplasm of root rhizodermal cells and the role of low-molecular-weight root exudates and siderophores in Fe acquisition of plants growing in soils of differing Fe availability is very limited (Marschner and Römheld, 1994); this suggests that there is a need to further investigate the buffering effect of Fe on root-induced differential uptake patterns. Such interactive investigations are conspicuously absent in the published literature. A similar situation exists with regard to the role of HCO_3^- ion in affecting Fe and Zn nutrition of crop plants. Mengel (1994) hypothesized that it is the HCO_3^- ion in association with the NO_3^- ion, found in calcareous soils, that trigger Fe chlorosis. The chlorosis is induced by the impaired Fe uptake from root apoplast into the cytosol of root cells in the presence of excessive HCO_3^- and NO_3^- ions, and a similar situation exists in the case of leaves. Reduction of apoplast pH by spraying chlorotic leaves with an acid, such as H_2SO_4, led to a regreening of the leaves. The hypothesis of Marschner and Römheld (1994) stresses the physiological effect, while that of Mengel (1994) stresses the chemical one. But in both cases, the possible Fe buffering effect vis-a-vis the root-induced changes merit much closer scrutiny than what has hitherto been attempted.

Parallel to the above studies, the role of excess HCO_3^- ion in the growth medium on Zn nutrition of wheat cultivars has recently been reported (Yang et al., 1994), indicating that excess HCO_3^- ion in the growth medium leads to accumulation of organic acids and their insufficient compartmentation in Zn-inefficient cultivars as compared to Zn-efficient cultivars. These studies point to the lacuna in a proper understanding of the buffering effects vis-a-vis organic acid accumulation. It is not known what effects Zn buffering in the medium would have on excess accumulation of the organic acids in the Zn-inefficient cultivars as compared to the Zn-efficient cultivars.

9. CONCLUDING COMMENTS AND FUTURE IMPERATIVES

Historically, soil testing has been used to quantify availability of essential plant nutrients to field-grown crops. However, contemporary soil tests are based on philosophies and procedures developed several decades ago without significant changes in their general approach. For a soil test to be accurate, one needs to clearly understand the physico–chemico–physiological processes at the soil–root interface, and an understanding of soils and plant root systems as

polycationic systems is essential. It is this knowledge that leads to sound prescriptive soil management practices inasmuch as nutrient availability vis-a-vis fertilizer application is concerned, because of all the factors which govern sustainability of crop production, the nutrient factor is the most important, yet, it is also the least resilient to management. This review focuses on the buffering power of plant nutrients, especially phosphorus, potassium, zinc, and some other heavy metals such as cadmium, on their availability to growing plants. Experimental evidence is presented from research carried on temperate (Central European and North European) and tropical soils (African and Asian soils) which unequivocally establishes the fact that precise quantification of the nutrient buffer power holds the key to a clearer understanding of the plant availability of some of the more important essential plant nutrients, such as phosphorus, potassium, and zinc. The Nutrient Buffer Power Concept attempts to explain availability of plant nutrients on the basis of the diffusion model, as it is the principal process by which phosphorus, potassium, and zinc are taken up by plant roots. Possibly, other nutrients which are taken up by plant roots by the same process would also conform to the principles of this concept. To substantiate this, supportive experimental evidence is needed.

There are similarities between the buffer power approach and quantity–intensity (*Q/I*) approach in predicting plant availability of important nutrients such as phosphorus and potassium. While the *Q/I* approach has met with a fair measure of success in predicting P availability, with regard to K availability the *Q/I* relationship does not enjoy universal acceptance since a single relationship for all soils between K uptake by a given crop and AR_K does not exist, perhaps due to the nature of the soil components regulating AR_K.

In substance, soil testing in a laboratory is meant to simulate what a plant root would accomplish in a field soil. All soil tests meet this requirement with different degrees of success. But, for a soil test to be universal in scope, it must attempt to quantify, as precisely as possible, factors which most crucially affect plant root uptake. Of all the factors involved in nutrient uptake, the most crucial is the average nutrient concentration on the root surface. In a dynamic state of plant growth it is virtually impossible to quantify precisely the average nutrient concentration on the root surface. The nutrient's buffer power is an indirect measure of the average nutrient concentration on the root surface, and analytical methods which quantify the buffer power with precision would render the soil test in question dependable; hence, the fertilizer recommendation which follows would be reproducible. It is against this background that The Nutrient Buffer Power Concept merits wider application for field use. Fertilizer prices have dramatically escalated following the oil crisis of the

mid-1970s, and field experience shows that recommendations emanating from routine soil tests have met with only limited success. A number of countries on the Asian and African continents spend enormous sums of money on importing fertilizers, which is a great strain on their national exchequers. Most of these countries have no infrastructure for fertilizer manufacture and where there is any, the soil testing support service is far from satisfactory. Since fertilizer is a crucial input, second only to water, in modern farming, cost-effective fertilizer recommendations are an important prerequisite for successful agriculture. In countries such as India, fertilizer prices, especially of phosphate and potassium, have skyrocketed following governmental policies centered on a market economy. In such situations, farmer confidence can only be instilled and maintained by accurate soil testing and reproducible fertilizer recommendations.

The success of a new approach, to a large measure, rests with the ingenuity of those applying it to suit the demands of a new situation. This principle is no exception in making the "Nutrient Buffer Power Concept" a universal success. As compared to routine soil testing, this approach calls for the accurate determination of the buffer power of the nutrient in question, to begin with. Once this is done, the buffer power factor can be integrated with the routine soil test data and fertilizer recommendations can be made on the basis of this new information. This implies that, in addition to obtaining routine soil test data, one also needs to know the buffer power. This review has shown how the buffer power is determined based on analytical methods varying from a simple adsorption–desorption equilibrium technique to elaborate EUF. Only selected laboratories around the world have EUF facilities. Where they are absent, alternative analytical procedures to precisely quantify the buffer power need to be developed. Developing appropriate procedures to quantify the buffer power and modification of the protocol for routine soil testing to integrate buffer power data for precise fertilizer recommendations calls for both ingenuity and drive on the part of the researcher, but that will be the future imperative of accountable soil testing.

ACKNOWLEDGMENTS

With love I dedicate this chapter to my wife, Pankajam, who sustains me in this very difficult journey that life is.

Addendum. "The Nutrient Buffer Power Concept" project was shortlisted for the very prestigious U.S. $1 million Rolex Awards for Enterprise 2012 for its originality from more than 3500 nominations worldwide and is the only project selected for this coveted distinction from the Asian continent.

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INDEX

Note: Page numbers followed by "*f*" indicate figures, and "*t*" indicate tables.

I

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